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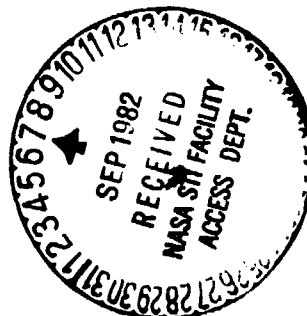
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# Gas Turbine Critical Research and Advanced Technology (CRT) Support Project

## FY 1980 Annual Report

Edward R. Furman, David N. Anderson, Michael A. Gedwill, Jr.,  
Carl. E. Lowell, and Donald F. Schultz  
National Aeronautics and Space Administration  
Lewis Research Center

July 1982



Prepared for  
**U.S. DEPARTMENT OF ENERGY**  
**Fossil Energy**  
**Office of Coal Utilization**

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U.S. DEPARTMENT OF ENERGY  
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# GAS TURBINE CRITICAL RESEARCH AND ADVANCED

## TECHNOLOGY (CRT) SUPPORT PROJECT:

### FY 1980 ANNUAL REPORT

Edward R. Furman, David N. Anderson, Michael A. Gedwill, Jr.,  
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#### SUMMARY

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This report summarizes the technical progress made during FY 1980 in the Critical Research and Advanced Technology Project (CRT). The program is to provide a critical technology data base for industrial/utility gas turbine systems that are capable of burning coal-derived fuels in an economical and environmentally safe manner. Two prior Annual Reports have been published, FY 1978 and FY 1979, and each included a number of subtasks which were completed and summarized in the reports. For completeness in reporting project status, these prior results are included in this report.

The utilization of coal-derived liquid fuels in gas turbine systems could be inhibited by the presence of two undesirable constituents in this class of fuels. The first is fuel bound nitrogen (FBN) which is typically high in these fuels and which is readily converted to oxides of nitrogen ( $\text{NO}_x$ ) in the combustion process. The second element of concern is the presence of trace metal contaminants that can contribute to hot corrosion and/or fouling of the turbine hot section materials.

To address these potential problems, the CRT project has been organized to investigate technology for the turbine hot section parts and to deal with the FBN and trace metal contaminants in the fuel. A combustion development task composed of four subtasks is underway to address the first problem. The first subtask has as its objective the conduct of a literature survey to accomplish the systematic assembly of existing data on the elemental composition, structural characteristics, and the physical and chemical properties of liquid and gaseous coal-derived synthetic fuels. A final report on this subject is being written and will be published in FY 1981.

The second subtask,  $\text{NO}_x$  Emission Modeling, has as its objective the analytical determination, through combustion modeling, of how combustor operating conditions affect the conversion of FBN to  $\text{NO}_x$  when burning synthetic fuels which contain significant quantities of organic nitrogen compounds. An adiabatic stirred-reactor model was developed which predicted several of the important trends for the emissions from two-stage (rich-lean) hydrocarbon combustors. This activity was completed in FY 1980 and a final report will be published in early FY 1981.

The third subtask, Flame Tube Experiments, was initiated to experimentally evolve fundamental combustion concepts for minimizing the conversion of FBN to  $\text{NO}_x$ , and to provide verification of the  $\text{NO}_x$  Emission Model. Rich-lean two stage combustion was shown to successfully reduce FBN to  $\text{NO}_x$  conversion to less than 10 percent for a FBN content of 0.5 to 1.0 percent and a primary zone equivalence ratio of 1.5 to 1.7. This result was predicted by the  $\text{NO}_x$  Emission Model. This activity was completed in FY 1979.

The fourth subtask in the combustion development task is Combustor Sector Tests. The objective of this effort is to evolve and evaluate experimental combustors which are capable of burning coal-derived fuels in an environmentally acceptable manner. Two variable geometry combustor sectors are being designed and fabricated for these tests. Sector testing is scheduled to begin in mid-1981.

A second task, Long Life Materials - Corrosion Resistance, was initiated to address the problems of hot corrosion, and excessive deposition, or fouling of the turbine hot parts which are caused by trace metals in the coal-derived fuels. The first subtask, Fuel Corrosivity Prediction, was initiated to evaluate the resistance of high strength superalloys to potential fuel impurities and to evaluate additives and additive techniques for the reduction of the corrosive effects of such impurities. Doped fuel tests of simulated coal-derived fuels were conducted in a Mach 0.3 burner rig. From the test data obtained over the time period of 1978 to 1980, an empirical base for a hot corrosion attack analytical model was developed. The test parameters which were varied in accordance with a statistical design were dopant concentrations and combustion temperatures. A computer program was developed which is unique and which has been enlarged to include most fuel impurities common to this class of fuels and a number of typical turbine alloys. The program is available for use by others. In the second subtask, Additive Tests, barium was identified as having potential for reducing hot corrosion caused by sodium sulfate. This beneficial result is attained by the formation and deposition of barium sulfate on the hot surfaces. Additional tests verified that the noncontinuous application of barium and/or strontium can provide an effective hot corrosion barrier for periods up to twice the application time period. An intermittent application approach is thus suggested. Actual Fuel Tests, subtask 3 for this development activity, were conducted using two fuels, an SRC-II naptha and a micronized coal-oil mixture. Results of these tests indicate that limited potential for hot corrosion is likely to exist because of the low sodium and potassium levels in the fuels, but that deposition and fouling is likely to be a problem for this class of fuels. Combustion experience with SRC-II naptha in this test series indicates that several potential problem areas exist which involve: storage stability of the fuel; reaction of fuel components with storage and transfer hardware; and operational problems. The operational problems included filter clogging and hot section fouling caused by deposits composed of trace metal compounds. The combustion of the micronized coal-oil mixture resulted in the formation of extensive deposits. These deposits resulted from the transformation of coal minerals to ash. The tests were concluded after 45 hours of operation due to the expenditure of available fuel.

Another subtask, Deposition and Fouling, was initiated to make thermodynamic predictions of the composition and dew points of the deposits formed from the combustion of coal-derived fuels. An equilibrium thermodynamic analyses was performed using a LeRC Complex Chemical Equilibrium Calculation Program. This program data base was extended and the predictions of the program reliably identified the type of depositions one could expect when burning coal-derived liquids. The modified program is unique and is available for use by others. The final undertaking for this task was initiated to examine the potential for plugging of advanced cooling systems on airfoils of turbines operating on coal-derived liquids. At test conditions employed and with practical and acceptable cooling air flow rates to the airfoils, severe hole plugging was experienced. In addition, the effect of increased

operating pressures on deposition was studied. Calculations indicate that the deposition rate will increase with an increase in operating pressures. Thus, increased deposition and airfoil cooling hole plugging may be anticipated at current turbine operating pressures.

Thermal Barrier Coatings (TBC) were identified as a possible approach which could be used to solve the hot corrosion problem. This task was divided into three elements. The first was aimed at determining the effects of operating parameters and fuel contaminants on TBC life. The tests were conducted in two Mach 0.3 burner rigs and included variations in test parameters, TBC composition and thickness, and in bond coat composition. Supporting tests were conducted to improve the oxidation and corrosion resistance of the bond coat and the adherence of the TBC to the bond coat. In addition, reaction studies were conducted to determine if and how the TBC powders react with air impurities and with combustion product compounds. Significant improvements in TBC system durability were attained. All of these tests are complete and reports are being written.

A third task, Technology Evaluation Studies, was initiated to investigate the impacts of various technologies on system performance, to evaluate alternative system concepts and program options and to support the DOE program objectives through technical evaluations, as required. Three studies were completed: Thermal Barrier Coating-Liquid Cooling Study; Thermal Barrier Cooling-Low Critical Alloy Study; and a Fuel/Stack/Temperature/Performance Study. Significant benefits were identified in each of the technology development areas. The benefits and costs for the various concepts are discussed in this report, as well as, in the individual published reports.

A fourth task element, Catalytic Combustors, was initiated in FY 1979. The purpose of this task was to evaluate the possible use of catalytic combustors in industrial/utility gas turbine applications. The testing included heavy oils and coal-derived fuels. An endurance test of a catalyst burning No. 2 distillate oil at 5 atmospheres pressure and 2300° F was run for 1000 hours. This test, which was performed under contract by Englehard Industries, achieved limited success. Prevaporized fuel testing of heavy fuels using heated air was conducted in-house. Some difficulty was encountered in effecting fuel vaporization. With careful control of the heated inlet air and the use of a graded cell reactor (large cells at the inlet followed by fine cells) the tests were successfully concluded. Combustor tests employing liquid fuel droplets (incomplete vaporization) were initiated under contract. Limited testing was performed during this fiscal period. The catalytic combustion of coal-derived gases is planned for 1981.

## INTRODUCTION

The Critical Research and Advanced Technology Support (CRT) Project was initiated between NASA and the ERDA, Office of Fossil Energy, with the signing of Interagency Agreement No. EF-77-A-01-2599 on June 30, 1977. Upon creation of the Department of Energy (DOE) on October 1, 1977, the project was assigned to the DOE, Division of Power Systems, which was subsequently renamed the Office of Coal Utilization. This project was formulated to provide a gas turbine critical technology data base which could be utilized in the development of improved gas turbine power conversion systems for coal and coal-derived fuels. This project is coordinated with the DOE Advanced Conversion Technology (ACT) Program and the advanced gas turbine program of the Electrical Power Research Institute (EPRI). The current CRT project en-

deavors are covered under Interagency Agreement DE-AI01-77ET-10350, dated October 30, 1980. The planned technical activities will be completed in FY 1981 and all reporting will be completed in FY 1982.

The focus of the effort in this project has been on "critical" technologies - those problems that must be resolved before coal-derived fuels can be considered viable for use in gas turbines. Two technologies have been identified for inclusion in this effort: combustion and materials. Emphasis in the combustion task is on reducing both thermal and fuel bound  $\text{NO}_x$  emissions. Emphasis in the materials task is on protecting turbine hot section materials against trace metal contaminants in coal-derived fuels, which can lead to unacceptable hot corrosion. Several approaches to solving the hot corrosion problem are being investigated, including developing a hot corrosion life model and using fuel additives or protective coatings. Systems studies were made to help integrate and guide the materials and combustion tasks.

The technical objectives of the CRT project are:

- (1) To develop combustor concepts that can burn coal-derived fuels in an environmentally acceptable manner.
- (2) To develop a hot corrosion data base for materials exposed to combustion products of coal-derived fuels and to correlate these data in a hot corrosion life prediction model.
- (3) To develop ceramic coatings that provide protection against hot corrosion and that have acceptable life in coal-derived fuel combustion products.
- (4) To study the trade-offs among various gas turbine technologies, operating conditions, and component designs.

The following sections discuss the purpose of each task, the technical approach to its accomplishment, and major results and conclusions obtained to date. For results attained during FY 1980 figures and tables are included to describe these results. For work completed prior to 1980, the efforts are summarized without figures but refer to figures in previously published reports. References providing a detailed discussion of previous results are included, where appropriate.

## TASK 1.0 - SYNCRUDE AND SYNFUEL CHARACTERIZATION AND COMBUSTION STUDIES

The objectives of this task are (1) to establish a data base of the properties of coal-derived fuels (Subtask 1.1) and (2) to evolve combustion technology so that these fuels can be used in utility/industrial gas turbines with minimum  $\text{NO}_x$  emissions (Subtasks 1.2, 1.3, and 1.4). This task is also planned to provide data to aid in establishing fuel specifications for advanced gas turbine systems burning coal-derived fuels in an environmentally acceptable manner. Each subtask is described in the following section.

### SUBTASK 1.1 - SYNCRUDE AND SYNFUEL CHARACTERIZATION

The objective of this subtask is to assemble in a systematic manner existing data regarding physical, chemical, elemental composition and structural characteristics of synthetic fuels derived from coal. The major activities consist of literature surveys and the evaluation of available data on coal-derived liquid and low Btu gas fuel properties. Survey results are being completed in the following categories:

(1) Compilation of existing property data on coal-derived fuels of greatest interest, as well as, the associated coal conversion processes.

(2) Formulation of data base tables in which fuel properties, a bibliography of reference sources and fossil energy contract numbers are tabulated.

(3) Provision of summary material which includes fuel property data tables by distillate categories, data plots indicating trends in synfuel properties irrespective of process type and the identification of fuel characterization data which is required but not available in the literature.

The survey emphasizes, but is not limited to, DOE-sponsored coal-derived fuel production pilot plants. Fuel processing or characterization by NASA is not included as part of this effort.

A literature survey was conducted in 1978 and has been published as DOE/NASA/2593-79/8 (ref. 1). Summary plots from this report may be found in figures 1 to 3 of DOE/NASA/2593-24 Report (ref. 2). Very little detailed, comprehensive characterization data existed at the time of this survey. There is, however, considerable current activity in synthetic fuels programs. These programs will be reviewed and a literature survey update of fuel properties will be published in FY 1982.

#### SUBTASK 1.2 - NO<sub>x</sub> EMISSION MODELING

The primary objective of this work is to analytically determine, by computer modeling, the effects of combustor operating conditions and geometry on the conversion of fuel bound nitrogen into oxides of nitrogen (NO<sub>x</sub>). For this purpose, the NASA-Lewis General Chemical Kinetics Program was modified to perform adiabatic stirred-reactor model computations. Nonlinear algebraic equations for multicomponent, chemically rate limited homogeneous reaction in a perfectly-stirred reactor were used. These equations were programmed and incorporated as a subroutine into the general chemical kinetics program (ref. 3). Computations were performed for a wide range of conditions. Emphasis was on a rich-burning primary stage followed by air dilution and lean second-stage burning. This is the condition for minimum NO<sub>x</sub> formation. The fuels used and other operating conditions were chosen to match, as closely as possible, those used in the experimental two-stage flame tube study of subtask 1.3 (reference 4). This was done to determine if the simple two stage stirred-reactor model which is chemical rate controlled can predict the trends observed in the flame tube for NO<sub>x</sub> and carbon monoxide formation. The flame tube combustion is controlled by a combination of chemical reaction, heat transfer, and turbulent mixing processes. All computations and two stage flame tube tests (Subtask 1.3) have been completed and the results (reference 5) will be reported at the 26th International Gas Turbine Conference, March 1981.

Three different fuels were used to vary the fuel hydrogen content from 9 to 18 percent by weight. They are:

- (1) Pure propane (18 percent hydrogen)
- (2) A propane-toluene mixture containing 11 percent hydrogen
- (3) Pure toluene (9 percent hydrogen)

Computations and tests were performed using fuel bound nitrogen contents (as nitrogen atoms) of 0, 0.5, and 1.0 percent by weight. The primary equivalence ratio was varied over the range of 0.6 to 1.8 and secondary equivalence ratio was held constant at 0.5. Pressure was constant at 0.48 MPa (5 atmospheres) for most of the computations. However, a series of computations



for propane-toluene combustion at 12 atm were performed to predict the effect of increased pressure. Results show that increasing pressure causes a moderate increase in  $\text{NO}_x$  concentrations at most primary equivalence values.

A chemical model with 91 reaction steps was used to model the oxidation of propane and toluene and the formation of oxides of nitrogen. The results of the analytical study and experimental comparisons are as follows:

(1) The simple stirred-reactor model was able to predict several of the important trends for the emissions from two-stage hydrocarbon combustion.

(2) Two-stage, rich-lean combustion gives experimental conversion rates of fuel bound nitrogen to  $\text{NO}_x$  of 10 percent or less for rich equivalence ratios of 1.5 to 1.7 and fuel bound nitrogen contents of 0.5 and 1.0 percent by weight. These results of the experimental flame-tube work are the same as those predicted by the two-stage well-stirred reactor computations.

(3) Both experiment and theory show that decreasing fuel hydrogen content causes a small increase in  $\text{NO}_x$  emission level. The presence of fuel nitrogen may decrease the effect of hydrogen content on  $\text{NO}_x$ .

(4) Although the absolute level of  $\text{NO}_x$  emission increases with fuel bound nitrogen content, the percent conversion of the fuel nitrogen decreases slightly as the amount of fuel nitrogen increases. This is found both experimentally and theoretically.

(5) Both experimentally and theoretically, the rich primary equivalence ratio for minimum  $\text{NO}_x$  formation shifts to higher values as the amount of aromatic hydrocarbon (toluene) in the fuel is increased. This can be explained by the reaction of the pyrolysis products of toluene directly with NO to increase the NO destruction rate.

(6) Carbon monoxide emissions increase significantly with decreasing fuel hydrogen content, as shown by both the experiments and the theoretical computations. Also CO emissions are highest at the rich primary equivalence ratios that give minimum  $\text{NO}_x$ . This fact, along with limited measurements indicating relatively high smoke emissions, indicates that tradeoffs will be necessary between the conditions that minimize  $\text{NO}_x$  and those that control CO and smoke emissions.

(7) Both experiments and theoretical computations show that carbon monoxide emissions are independent of fuel bound nitrogen content.

(8) From theoretical computations the formation of  $\text{NO}_x$  increases slightly at most primary equivalence ratios when the pressure is increased from 5 to 12 atm. The increase is between 3 and 30 percent at the rich equivalence ratios for minimum  $\text{NO}_x$  formation. All of the increase is due to the formation of thermal  $\text{NO}_x$ . The percent conversion of fuel bound nitrogen at 12 atm is slightly less than at 5 atm.

(9) Computed  $\text{NO}_x$  emissions are essentially independent of secondary residence time for all fuels used, when the secondary equivalence ratio is 0.5.

(10) Computed CO emission decreases significantly as secondary residence time increases for all fuels used and all operating conditions.

(11) Computed  $\text{NO}_x$  and CO emissions are independent of primary-zone residence time. Experimental  $\text{NO}_x$  emissions, however, increase moderately with primary residence time.

### SUBTASK 1.3 - FLAME TUBE EXPERIMENTS

The objectives of this subtask were to experimentally measure the performance of various combustion concepts which were designed to minimize the

conversion of fuel bound nitrogen to  $\text{NO}_x$ , to determine achievable baseline levels of fuel bound nitrogen conversion to  $\text{NO}_x$  and to provide verification of the Subtask 1.2 analytical model. Fundamental flame tube combustion experiments, including two-stage combustion with independent airflow control to each stage, have been conducted and combustion and emissions data have been recorded. Test series for ranges of stoichiometric burning conditions were conducted with gaseous propane fuel, propane with pyridine addition, toluene fuel, toluene-propane blends, toluene-propane-pyridine mixtures and with SRC-II naphtha and SRC-II mid-distillate liquid fuels.

The technical effort for this subtask has been completed and the results published in reference 4. A schematic drawing of the test rig, illustrating flow, geometric and measurement parameters of interest is contained in figure 1 of reference 4 and photographs of the test rig and combustion sections are contained in figures 6 and 7, respectively. In operations, air at 670 K (750° F) and 0.48 MPa (75 psia) was premixed with fuel, burned at primary equivalence ratios of 0.5 to 2.0 and secondary equivalence ratios ranging from 0.5 to 0.7. Fuel blends were proportioned to vary hydrogen composition from 9.0 to 18.3 percent and fuel nitrogen composition from 0 to 1.5 percent. Distillates of coal syncrude produced by the SRC-II process were also tested, and the results compared to the data obtained with the propane-toluene-pyridine fuel blends. In addition to oxides of nitrogen, the exhaust gas was sampled for carbon monoxide, carbon dioxide, unburned hydrocarbons, and smoke. Among the more significant results obtained were the following:

- (1) Rich-lean two-stage combustion successfully reduces fuel bound nitrogen to  $\text{NO}_x$  conversion as compared to single stage combustion. Conversion rates of less than 10 percent can be achieved at optimum primary burning zone conditions. This result is shown in figure Nos. 16 and 18 of reference 4. Illustrated are plots of percent fuel nitrogen conversion to  $\text{NO}_x$  as a function of primary zone equivalence ratio, for three fuel nitrogen concentrations. For lean burning conditions, conversion of fuel nitrogen to  $\text{NO}_x$  is significant - 35 to over 60 percent. For rich burning conditions significant amounts of fuel nitrogen are converted to elemental nitrogen with correspondingly lower conversion to  $\text{NO}_x$ .

- (2) The optimum primary equivalence ratios ranged between 1.4 and 1.7. The optimum secondary equivalence ratio for these tests was about 0.5. These values resulted in minimum  $\text{NO}_x$  production at combustion efficiencies of 99 percent or more.

- (3) Fuel hydrogen content had some effect on the optimum primary equivalence ratio. Decreased hydrogen content shifted the optimum primary operating conditions to richer values, as illustrated in figure 18 of reference 4.

- (4) Exhaust  $\text{NO}_x$  levels always increased with additional fuel nitrogen, however, increased fuel nitrogen levels reduced the percentage of fuel nitrogen to  $\text{NO}_x$  conversion.

- (5) Rich burning combustion systems, while controlling fuel nitrogen conversion to  $\text{NO}_x$  may also produce larger smoke concentrations than lean burning systems. Sufficient data to quantify this effect were not obtained in these tests which were confined to low pressure operation of five atmospheres or less, due to test facility limitations. In Subtask 1.4 testing, which will be conducted at high pressure conditions, rich burn smoke levels will be more fully explored.

#### SUBTASK 1.4 - COMBUSTOR SECTOR TESTS

The objective of this subtask is to evolve and evaluate experimental combustors capable of burning coal-derived fuels in an environmentally acceptable manner. Combustor testing will be conducted at representative industrial/utility gas turbine temperatures and pressures (idle conditions:  $T_{air\ in} = 260^\circ\text{F}$ ,  $P = 40\text{ psia}$ ,  $T_{out} = 975^\circ\text{F}$ ; peak conditions:  $T_{air\ in} = 735^\circ\text{F}$ ,  $P = 175\text{ psia}$ ,  $T_{out} = 2100^\circ\text{F}$ ) over an entire simulated load range from engine idle to peak power. Distillate fuels, heavy oils, doped heavy oil fuels and coal-derived fuels (as available) will be tested. Combustion efficiency, liner temperatures, exit temperature distributions, gaseous emissions, smoke levels, and deposit characteristics will be investigated. Tests will be run with thermal-barrier coatings on the inside of the combustor liner to determine their effects on performance and durability. Various levels of combustor technology will be evaluated to assess the degree of complexity required to achieve adequate emissions and performance. Existing combustor hardware, advanced variable geometry combustor concepts, and combustion concepts currently beyond present state-of-the-art, will be tested. This testing will be completed in 1981.

#### TASK 2.0 - LONG-LIFE MATERIALS CORROSION RESISTANCE

Coal-derived fuels contain varying amounts of trace metals, some of which may lead to hot corrosion or excessive deposition and fouling in the gas turbine hot section. Task 2.0 was undertaken to contribute to the evaluation and prevention of hot corrosion and to determine the extent and possible consequences of deposition and fouling.

#### SUBTASK 2.1 - FUEL CORROSIVITY PREDICTION

Subtask 2.1 was performed to predict and evaluate the resistance of high-strength super-alloys to potential fuel impurities using doped clean fuels and coal-derived liquids. This work was also carried out to predict and evaluate additive techniques for the reduction of the corrosive effects of such fuel impurities.

#### SUBTASK 2.1.1 - DOPED-FUEL TESTS

Doped-fuel tests were run with simulated coal-derived fuels. In these tests, selected contaminants were added to a clean fuel (1) to isolate the corrosion effects of a given contaminant and its concentration, and (2) to determine the interrelationships of time, temperature, and corrodent on hot corrosion. In FY 1980 all of the data obtained over the period FY 1978 to the present were evaluated and combined into an empirical hot corrosion attack model. The data accumulated from these tests are presented in detail in reference 6. The parameters, which were varied in accordance with a statistical design, were the dopant concentrations and the temperature. The dopants were sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and chlorine (Cl). The concentrations varied from approximately 0.01 wppm to 10 wppm. The ranges are shown schematically in figure 1. The gas temperature was varied between 800 and 1100°C (1472 and 2012°F). There were 322 points per alloy. The metal recession data from these experiments were fit to a polynomial equation using multi-linear regression. The final model was chosen by a backwards elimination type of regression.

Figures 2 through 6 illustrate the effects of the various impurities on corrosive attack and are derived from the model. In figure 2 we have K at 0.9 ppm, Mg and Ca at 0.1 ppm, Cl at 2.93 ppm, the temperature at 950° C (1742° F) and the time at 100 hours. Predicted metal recession as a function of Na concentration for each of the four alloys is plotted. Indications of the reliability of the predictive equations are provided by estimates of the standard deviation limits on the figures. In figure 3, a similar plot of metal recession versus Na concentration is presented. However, the Mg and Ca concentrations are increased to 1.0 ppm. A comparison of the two plots shows a general reduction in attack for all alloys with the greater concentrations of Mg and Ca. The reduction is minimal for Mar M-509; it is substantial for IN-100, U-700, and IN-792. Figures 4 and 5 provide similar plots to indicate the effects of Mg and Ca on potassium attack. In general, the same observations can be made: K causes increasing attack with increasing concentration; Mg and Ca tend to reduce such attack. Figure 6 shows the effect of temperature on attack with the other variables held at their nominal center point values, that is, Na and K at 0.9 ppm, Ca and Mg at 0.47 ppm, Cl at 2.93 ppm, and the time at 100 hours. The metal recession of IN-100 decreases with increasing temperature; the metal recession of Mar M-509 increases slightly with increasing temperature; and both IN-792 and U-700 metal recession curves reveal maxima.

The model was successful in predicting erosion up to 500 hours of time. The correlation at 1000 hours and beyond was not satisfactory due to the simple  $\log_{10}$  (time) assumption of the model compared to the complex shape of a hot corrosion curve.

#### SUBTASK 2.1.2 - ADDITIVE TESTS

In FY 1978 barium was identified as an additive with great potential for reducing hot corrosion caused by sodium sulfate. However, the mechanism by which barium reduced or eliminated hot corrosion involved the deposition of a layer of barium sulfate. The object of the work in 1979 was to maintain the desirable inhibiting effects of barium while reducing the amount of deposition of the inert sulfate. Two approaches were evaluated. In the first, various elements were added with the barium. In the second, attempts were made to add the barium during only part of the exposure. As in the case of the doped fuel work, the tests were carried out in Mach 0.3 burner rigs and the alloys used were IN-100, U-700, IN-792, and Mar M-509.

The results of the elemental additions are summarized in Table II of reference 2. In general, most of these additions resulted in increased hot corrosion, especially on IN-100, even though in some cases the apparent deposition rates decreased. The addition of elemental silicon resulted in a substantial reduction in deposition (a factor of 2) and little increase in corrosion. Even here some slight increase in attack was noted in IN-100. Strontium was very effective in retaining corrosion resistance, but did not reduce the amount of deposition.

The results of the intermittent application of the inhibitor are summarized in Table III of reference 2. In brief, these data indicate that an addition of barium and/or strontium can be discontinued and the alkaline earth sulfate deposit will remain an effective barrier to hot corrosion for some period of time. In these tests, a 40 hour treatment was beneficial for approximately 40 additional hours. This would indicate that such an intermittent application approach could be used to prevent excessive buildup

of the inert sulfate while retaining the full hot corrosion resistance of the additive. This work is described in more detail in reference 8.

### SUBTASK 2.1.3 - ACTUAL FUEL TESTS

Two types of fuels were utilized in these tests. One was the SRC-II naphtha fuel, while the second was a micronized coal-oil mixture. The compositions of these fuels are shown in Tables I and II. For both fuel types, extensive modifications had to be made to the burner rig in order to get them to burn consistently. These extensive modifications are detailed in references 9 and 10. Burning of the fuels was difficult, even after the modifications. The test of the SRC-II naphtha was limited to approximately 190 hours while the test of the micronized coal-oil mixture was limited to about 45 hours because of fuel availability. In both cases, the Na and K levels in the fuel were low enough as to lead one to predict essentially no hot corrosion attack based on the work described above. This was, indeed, the case as is shown in figures 7 and 8. The microstructures confirm that the corrosion attack is the same as that found in oxidation tests, and also show extensive deposits formed on the surfaces of the samples. Thus, the conclusion drawn from this work is that while no potential for hot corrosion is likely to exist, deposition and fouling is likely to be a problem when using these fuels.

### SUBTASK 2.2 - DEPOSITION AND FOULING

This subtask has two objectives: (1) to make thermodynamic predictions of the composition and dew points of deposits formed from the combustion of coal-derived fuels, and (2) to determine the potential for plugging of advanced cooling systems on airfoils of turbines operating on coal-derived liquids.

#### SUBTASK 2.2.1 - COMBUSTION PRODUCT ANALYSIS

These tests were performed in a Mach 0.3 burner rig equipped with a special platinum target. Four cuts of SRC-II fuels were used in this test. One was a naphtha, the second a light oil, the third a wash solvent, and finally a mid-heavy distillate blend. The analyses of these fuels are shown in Table I. The major metallic elements which contributed to the deposits were copper, iron, chromium, calcium, aluminum, nickel, silicon, titanium, zinc, and sodium. The deposits were found to be mainly metal oxides (see Table III). An equilibrium thermodynamic analysis was employed to predict the chemical composition of the deposits. Agreement (see Table III) between the predicted and observed compounds was excellent. As a result, considerable confidence in the ability to determine deposit composition from thermodynamic considerations was gained. This work is detailed in ref. 9.

#### SUBTASK 2.2.2 - AIRFOIL COOLING HOLE PLUGGING

This work was undertaken to estimate the potential of cooling-hole plugging in the combustion environment of coal-derived fuels. Two airfoil cooling schemes were planned to be studied.

(1) Film cooling - airfoils with relatively large coolant holes and high coolant velocity. Tests of film-cooled blades were completed and a report was published (ref. 11).

(2) Transpiration cooling - airfoils with many small holes and low coolant velocity were planned. No transpiration-cooled airfoils were available, however, and these tests were not run.

The film-cooled-blade test results (ref. 11) are summarized here. Two types of fuel contaminant levels were chosen for the film-cooled-blade tests. These compositions are in parts per million in the combustion gas (20 to 30 times the levels expected in a typical coal-derived fuel). Dopant A proportions correspond to a typical coal-derived fuel such as SCR-11; dopant magnitudes were chosen to accelerate testing. Dopant B is exactly the same as dopant A, except for the 0.5 ppm phosphorus. Phosphorus was noted from prior in-house testing to be extremely critical in terms of deposit "stickiness." Thus, small quantities of phosphorus can lead to rapid deposit buildup and hole plugging. Phosphorus has not been detected in fuel trace metal analyses to date. However, phosphorus deposits were detected, even though it was not thought to exist in the fuel. A possible explanation for this apparent contradiction is that, when the fuel is analyzed for trace metals, the phosphorus is lost - through volatilization, for example.

In the test rig, doped hot gas from the burner rig was directed onto the leading edge of a film-cooled turbine blade. Film-cooling holes on the blade were distributed around the leading edge in a typical "showerhead" configuration. Cooling air for the blade was ducted into the blade and then forced out through the film-cooling holes. The flame temperature was varied and the leading-edge temperature was adjusted at the start of each test to 815° C (1500° F) by adjusting the coolant flow rate. The coolant pressure was then fixed; and, as the cooling holes became plugged, the coolant flow decreased and the leading-edge temperature increased. The change in leading-edge temperature was monitored.

The results of these tests are summarized as follows:

(1) The tests that were run with coolant mass flow/hot gas mass flow < 1 showed severe hole plugging.

(2) Dopant B (with 0.5 ppm P) was worse than dopant A.

(3) For coolant mass flow ratios (>1.0), hole plugging can be nearly eliminated, depending on the fuel composition. These coolant flow quantities and pressure requirements may not, however, be practical.

The effect of pressure was also studied in reference 11. With a deposition kinetics theory developed by Rosner, et al., the deposition rate was calculated as a function of pressure. Figure 17 (ref. 11) shows the predicted deposition rate of sodium sulfate, which is typical of other deposits formed, as a function of pressure. These calculations indicate that deposition rate increases with pressure; thus, deposition and hole plugging problems at elevated pressures should be more severe than those observed in the atmospheric burner rig tests. Also, for a 10:1 pressure ratio turbine, the calculated deposition rates are about 10 times those at 1 atmosphere. Thus, rig dopant levels of 20 to 30 times actual levels should produce deposits in amounts approximating those in utility turbines over an extensive service lifetime.

### SUBTASK 2.3 - THERMAL BARRIERS

This subtask is divided into three major elements. The first is aimed at determining the effects of operating parameters on thermal barrier coating life. This includes determining the effect of fuel-to-air mass ratio (and hence, hot gas temperature), the effect of temperature gradient through the

thermal barrier, and the effect of bond coat or substrate temperature on overall thermal barrier coating system performance in a combustion environment generated by firing a clean fuel (jet A) doped to a fuel impurity equivalent of 5 ppm Na + 2 ppm V. The mode of failure and failure location of ZrO<sub>2</sub>-type thermal barriers were analyzed on the basis of dew and melting points of the condensates from Na and/or V-containing combustion gases. The second element is aimed at improving the bond coat layer to provide better thermal barrier adherence via improved bond coat hot corrosion and oxidation resistance. The third element involves an experimental study of the reactions of thermal barrier coatings with potential fuel and air impurities. Powders of two thermal barrier coating materials were reacted with equivalent amounts of potential fuel, air, and bond coat-derived impurities. Results from these elements form the basis for analyzing the coating failure mechanism and for developing more impurity-tolerant thermal barrier coating systems.

#### SUBTASK 2.3.1 - ADVANCED THERMAL BARRIER COATINGS

In FY 1978, a number of ceramic thermal barrier coatings were identified in a hot corrosion burner rig test as having improved resistance to fuel and air impurities. The results of those tests indicated a need to establish a larger data base on how operating parameters affect thermal barrier coating system performance. These parameters include the effect of (a) oxide thickness on durability in doped combustion gases, (b) fuel-to-air ratio on overall performance, (c) substrate and bond coat temperature on useful life in oxidation or hot corrosion, (d) bond coat composition on thermal barrier life, and (e) surface temperature and temperature gradient through the thermal barrier coating on coating life. Two Mach 0.3 burner rig test series were initiated in FY 1979, to establish the effects of some of these variables on thermal barrier coating life.

In the first Mach 0.3 burner rig test, thermal barrier coating thickness and bond coat composition were variables. Coated specimens (IN-792) were tested in an eight-specimen test fixture in a manner similar to a previously reported test series (ref.12). Testing conditions were as follows: fuel-to-air mass ratio of 0.046, distance of specimen from the burner nozzle of 3.18 cm (1.25 in.), gas calculated temperature of 1552° C (2825° F), ceramic surface temperature for a 15 mil yttria-stabilized zirconia coated specimen of 843° C (1550° F) and fuel impurity equivalent level of 5 ppm Na and 2 ppm V. In these tests, the flux of impurities to the specimens, which is a function of the amount of impurities in the fuel and fuel usage, was 15 percent greater than in the prior tests where the fuel-to-air ratio was 0.040. Also, the hot gas temperature was increased 180° C (325° F) while the specimen surface temperature was held at 843° C (1550° F). The cyclic conditions such as length of exposure and inspection intervals were the same as in the previously referenced tests, except that now specimens were cooled when out of the flame, with an external blast of air in addition to the internal cooling air. In view of these changes, the test is more severe. The results are summarized in figure 16 of reference 2. The coating failure criteria was spallation of 1/4 of the coating area in the hot zone of the leading edge.

Based on a preliminary analysis of the results of these tests:

(1) There appears to be a 3-to-4X improvement in the durability of both Ca<sub>2</sub>SiO<sub>4</sub> and ZrO<sub>2</sub>-based thermal barrier systems in the Na+V doped combustion flame when the thermal barrier thickness is reduced to 0.012 cm (0.005 in.) from 0.038 cm (0.015 in.). There is, of course, a proportional

reduction in temperature drop through the thermal barrier coating for a reduction in thickness.

(2) CoCrAlY bond coats appear to offer a 2-to-3X improvement in coating life compared to NiCrAlY bond coats for  $\text{Ca}_2\text{SiO}_4$  thermal barrier coating systems.

(3) The NiCrAlY bond coats, Ni-18Cr-12Al-0.3Y and Ni-31Cr-11Al-0.6Y (from the bond coat optimization task) appear to improve thermal barrier coating system durability about 2X in Na+V doped combustion gases compared to Ni-16Cr-6Al-0.31Y.

In the second Mach 0.3 burner rig test, three yttria-stabilized zirconias and the 0.8CaO-SiO<sub>2</sub> thermal barrier coatings were tested at three fuel-to-air mass ratios. The objectives of this effort were to determine how flame temperature (and thus combustion products) and temperature gradient through the thermal barrier coatings affect thermal barrier system performance in 5 ppm Na + 2 ppm V doped combustion gases. The multiple specimen testing was similar to the previously referenced tests, except that 1.27 cm (1/2 in.) O.D. Waspaloy specimens were used for this test. The results of this test are summarized graphically in figure 17 of reference 2. Each data point represents the test results of two or more specimens. The criterion for coating failure was spallation of 1/4 of the coating area from the specimen leading edge where the substrate temperature was maintained at 843° C (1550° F). The data indicate that the spall behavior of yttria-stabilized zirconia thermal barrier coatings are sensitive to changes in the fuel-to-air mass ratio and that  $\text{ZrO}_2 - 8 \text{ w/o } \text{Y}_2\text{O}_3$  coatings are more spall resistant in this type of combustion environment.

As the fuel-to-air mass ratio was changed from 0.039 to 0.049 the following occurred: the amount of fuel impurities increased 25 percent, the surface temperature of the ceramic was higher, and the temperature gradient through the coating was higher. Other possible effects of changing the fuel-to-air mass ratio were that new corrosive species might be formed or that the thermodynamic dew points of the condensates changed significantly. Completion of the analytical work and thermodynamic calculation of the dew points of the condensates should be helpful in determining which of the parameters that change as the fuel-to-air is altered most affect coating performance.

In order to provide a basis for understanding and analyzing the failure of thermal barrier coating systems when exposed to dirty fuel combustion products, previous tests of the NASA-Lewis thermal barrier coating system  $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{NiCrAlY}$  at Westinghouse and General Electric, and NASA-Lewis, have been reviewed and the results of this review published in DOE/NASA/2593-78/3 (ref. 12). The test series carried out at NASA-Lewis was the focus of the analysis since the coating was exposed to all of the possible temperature conditions that were expected. Coating failure and failure location were explained in the DOE/NASA/2593-79/7 report (ref. 13) in terms of the thermodynamic dew points and melting points of the condensates and the temperature distributions within the coatings for these three series of tests.

The response in NASA-Lewis tests of single  $\text{ZrO}_2\text{-12w/oY}_2\text{O}_3/\text{Ni-16Cr-6Al-0.6Y}$  coated air-cooled specimens to Mach 0.3 burner rig exposure with various levels of Na and V fuel contamination is summarized in figure 18 of ref. 2. This coating was originally developed for a clean fuel application. At the 5 ppm fuel equivalent sodium level, the coating failed in a short time (92 one hour cycles compared to 1300 1 hour cycles for 0.5 ppm equivalent sodium level) at a location outside the hot zone as shown in figure 19 of reference 2. With 0.2 and 2.0 ppm V, the coating failed in about 200 and 25



1-hour cycles, respectively. With vanadium in the combustion gases, failures occurred in the hot zone as shown in figure 20 of reference 2. When a fuel equivalent dopant level of 5 ppm Na + 2 ppm V was used, the coating also failed rapidly - in about 43 1-hour cycles. However, now the failure occurred both in the hot zone and out of the hot zone. The microstructure of the coating on this specimen after exposure is shown in figure 21 of reference 2, along with microstructure of the as-deposited coating. Here, as well as in the other tests, no bond coat corrosion was detected. In addition, coating failure in these tests occurred within the ceramic near the bond coat/oxide interface. This mode of failure is similar to failures observed in cyclic burner rig tests with clean fuels (ref. 13) and in mechanical tests (ref. 14).

The locations of the failures observed in these doped fuel tests were in qualitative agreement with thermodynamic predictions of condensate compositions and their dew points, melting points, and locations within the coating. These are summarized in Table IX of reference 2. The most severe conditions for a porous plasma-spray-deposited ceramic coating such as  $ZrO_2-12w/oY_2O_3$  occur when a corrosive liquid such as  $V_2O_5$  or  $Na_2V_2O_6$  can condense at the surface and completely permeate the coating. That is, the dew point  $T_{dp}$  is above the surface temperature,  $T_s$ , of the ceramic and the melting point,  $T_{mp}$ , is below the bond coat temperature,  $T_{bc}$ . This was the case with  $V_2O_5$  formed in the 0.2 ppm, 2 ppm and 5 ppm Na + 2 ppm V tests and  $Na_2V_2O_6$  formed in the 5 ppm Na + 2 ppm V test. The problem with fuel or air impurities should not be as severe if the condensed combustion product is not reactive with the ceramic coating. If the melting point of the condensate is above the dew point (i.e., the condensate is a solid), or if the dew point is below the bond coat temperature, the fuel contaminant may be harmless. The fuel contaminant may also be harmless if the dew point is less than the surface temperature. With 5 ppm Na in the fuel, the dew point of the non-reactive  $Na_2SO_4$  condensate was below the surface temperature in the hot zone. Failure occurred out of the hot zone where the dew point was above the surface temperature as illustrated in figure 22 of reference 2. With 0.5 ppm Na in the fuel, the dew point was below the bond coat temperature in the hot zone and below the surface temperature, but above the bond coat temperature elsewhere. Thus, this test was not more severe than an oxidation test.

#### SUBTASK 2.3.2 - BOND COAT OPTIMIZATION

The work in this subtask was aimed at improving the oxidation and corrosion resistance of the bond coating and the adherence of the thermal barrier coating. Three test methods were used to evaluate bond coatings. Two of the methods were cyclic furnace tests which were run to determine the durability of bond coatings alone (oxidation), and that of bond coatings used with thermal barrier coatings (endurance). The third method of evaluation was to test thermal barrier coating systems in a Mach 0.3 burner rig. The thermal barrier coating was always  $ZrO_2 12 w/o Y_2O_3$  applied to 0.038 cm (0.015 in.) thickness using the same conditions as in reference 15. Two exposure cycles were used. One consisted of 6 minutes in the flame followed by a 3 minute forced air cool down. In the other cycle, dwell time in the flame was increased to 1 hour. In both cases the leading face of the specimens came to  $1050^\circ C$  ( $1922^\circ F$ ) while the inward facing surface reached about  $1150^\circ C$  ( $2102^\circ F$ ). Furnace test results were summarized in the 1979 Annual Report (ref. 2). To

abstract, in endurance testing at 1012° C (1853° F), twenty-two bond coats were evaluated on B-1900 + Hf. The best bond coating was Ni-14Cr-14Al-0.1Zr, based on the time to thermal barrier crack initiation, specific weight change and post-test metallography. Of the eight bond coats evaluated on Mar M-509, a cobalt-base alloy, Ni-31Cr-11Al-0.6Y, was the best bond coating based on the previous criteria. In cyclic oxidation tests at 1100° C (2012° F), the best bond coats were either Ni-14Cr-14Al-0.1Zr or Ni-16Cr-13Al-0.4Y on B-1900 + Hf and Ni-31Cr-11Al-0.5Y on Mar M-509 (ref. 15). Burner rig tests carried out using an eight specimen carousel in a jet A fuel fired Mach 0.3 burner rig as illustrated in figure 9, confirmed the validity of the furnace test results in terms of bond coat composition and thickness selection and plasma spray deposition parameters. The specimens were Rene 41 (nickel-base superalloy) solid bars having a diameter of about 1.25 cm (0.5 in.).

Figure 10 illustrates that those bond coat compositions having the best cyclic furnace oxidation resistance gave the best thermal barrier coatings life in the burner rig test. For this series of tests, bond coatings were plasma sprayed to 0.015 cm (0.006 in.) thickness using a power setting of 20 kW and argon - 3.5 volume percent hydrogen arc gas. All ceramic coating failures occurred on the hotter inward facing surface of the specimens. With the better bond coatings, the ceramic spalled before the bond coatings were appreciably oxidized. TBC failure occurred in the ceramic coating close to the bond coat/ceramic interface. These features are illustrated in figure 11. Thus, life appeared to be limited by crack growth in the ceramic coating induced by a combination of thermal exposure and cyclic thermal stress.

The effects of bond coating thickness and plasma arc power level with two of the better bond coats are illustrated in figure 12. The benefits of increased power level and bond coat thickness are apparent for the Ni-14.1Cr13, 4Al-0.10Zr bond coating. The effects of dwell time in the burner flame were also investigated and compared with the results of another investigation where less power and no hydrogen was used during bond coat application (ref. 16). The results are summarized in figure 13. Substantial improvements in durability (about 3X) of the TBC were observed for both the long and short heatup cycles with the improved bond coat application procedure. One should note that if only thermal cycling were life controlling, the lines in the lower plot would have zero slope while those in the upper plot would have a slope of about 20. Since the latter slopes are about 2 with the conventional deposition and about 5 with the improved deposition procedure, it can be concluded that thermal cycling had a stronger influence on life than time at temperature. The thermal cycling influence decreases as the bond coat oxidation resistance improves. Again, improved bond coats exhibited negligible oxidative degradation at coating failure. Thus, under the conditions used in these tests, the time at temperature component appears to be associated with the ceramic coating. This is further substantiated by surface structural changes observed in the ceramic as a result of exposure. These changes (mudflat crack network development) were controlled to a greater extent by thermal exposure time than by the number of thermal cycles (ref. 15).

#### SUBTASK 2.3.3 - REACTION STUDIES

In support of the burner rig tests, studies were conducted to determine how calcium orthosilicate (actual composition was 1.8CaO-SiO<sub>2</sub>) and barium

zirconate powders react with potential combustion product compounds of major fuel and air impurities and with bond coating elements. The powder reactions were monitored as a function of time by X-ray diffraction. These reactions were studied at 1100° and 1300° C (2012° and 2372° F) for up to 400 and 200 hours, respectively. The results of these tests are presented in DOE/NASA/2593-79/9 report (ref. 17) and are summarized in Tables X and XI of ref. 2.

These tables list all the chemical compounds used and the products of their reactions with calcium silicate and barium zirconate at 1100° and 1300° C. They also include columns marked with the letters "N" or "Y" indicating that essentially no (N) reaction took place or that, yes (Y) there was a partial or complete reaction. The entry "unknown phase" was used when some lines of an X-ray diffraction pattern could not be attributed to any compound listed in the Powder Diffraction File Search Manual, Publications SMA-26, Joint Committee on Powder Diffraction Standards 1978. In general, the heat treatments at 1100° and 1300° C produced similar results. When reactions were observed, they were usually the same at both temperatures. If there was no reaction at 1100° C, there was generally none at 1300° C. The results of these reaction studies are summarized as follows:

- (1) The impurities that reacted with  $2\text{CaO-SiO}_2$  are  $\text{Na}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{MgO}$ ,  $\text{CoO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , and  $\text{V}_2\text{O}_5$ .
- (2) The impurities that did not react with  $2\text{CaO-SiO}_2$  are  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{O}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{BaSO}_4$ ,  $\text{NiO}$ ,  $\text{ZnO}$ , and  $\text{Fe}_2\text{O}_3$ .
- (3) The impurities that reacted with  $\text{BaZrO}_3$  are  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{V}_2\text{O}_5$ .
- (4) The impurities that did not react with  $\text{BaZrO}_3$  are  $\text{Na}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{O}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{CoO}$ , and  $\text{ZnO}$ .

Thus, monovalent or divalent oxides and sulfates did not react with barium zirconate. Similarly, calcium orthosilicate was not affected by sulfates, however, it was attacked by sodium, barium and cobalt oxides. Vanadium and phosphorous are impurities generally contained in industrial fuels and their pentoxides reacted readily with both barium zirconate and calcium orthosilicate.

### 3.0 - TECHNOLOGY EVALUATION STUDIES

#### SUBTASK 3.1 - THERMAL-BARRIER-COATING LIQUID COOLING STUDY

How thermal barrier coatings (TBC) affect the performance and cost of electricity (COE) of air-cooled, open-cycle gas turbine systems has been investigated (refs. 18 to 20). These studies indicate potential reductions in both fuel usage and COE for utility gas turbine systems that use thermal barrier coatings. The objective of this subtask is to quantify the performance effect for more advanced steam- and water-cooled gas turbine combined cycle systems that use thermal barrier coatings. A plasma-sprayed, duplex thermal barrier coating, consisting of yttria-stabilized zirconia outer layer and NiCrAlY bond coating was assumed.

Air-cooled cases, both with and without TBC, were included as a reference or baseline. Three cases were considered for each coolant. In the first two cases, the metal substrate temperature and turbine inlet temperature were assumed to be the same as for the case without TBC, and the turbine coolant flow rate was reduced. Coating thicknesses of 0.038 and 0.076 centimeter (0.015 and 0.030 in.) were assumed. In the third case, the metal temperature and the coolant flow rate were kept the same as for the case without TBC, and the turbine inlet temperature (TIT) was increased. A coating thickness of 0.038 cen-

timeter (0.015 in.) was used in this case. The bond coating thickness was assumed to be 0.010 centimeter (0.004 in.) for all cases. For the water-cooled combined cycle cases studied, turbine rotor-inlet temperatures were used (to be consistent with the DOE High Temperature Turbine Technology (HTTT) program). Turbine vane inlet temperatures for these conditions are 1448°C (2639° F) and 1684° C (3062° F), corresponding to rotor-inlet temperatures of 1425° C (2600° F) and 1650° C (3000° F), respectively. The combined cycle cases studied are shown in table I of reference 21.

The improvements in performance made possible by utilizing TBC's were studied for combined cycle systems using air, steam and water coolants. If a 0.038 cm (0.015 in.) thick TBC is utilized to reduce cooling fluid flow requirements (while maintaining the surface metal substrate and turbine inlet temperatures constant) the combined cycle efficiency can be improved by 0.5 to 1.5 percentage points and the specific power (kW/kg/sec) improved by up to 5 percent. On the other hand, if the same coating thickness is used and a constant cooling flow and increased turbine inlet temperatures are permitted, the cycle efficiency increases by 1.4 to 1.8 percentage points and the specific power increases approximately 30 percent.

### SUBTASK 3.2 - THERMAL BARRIER COATING-LOW CRITICAL ALLOY STUDY

The purpose of this study was to identify and quantify the potential cost savings that could result if the use of thermal barrier coatings on gas turbine hot section components permitted the decreased use of strategic alloys in these components. By providing insulating protection between the corrosive hot gases and the metallic load carrying members, the use of TBC's allow the metal substrate temperatures to be reduced. At the lower substrate temperatures, corrosion problems are reduced while material strength increases. Thus, some tradeoff may be made between turbine materials used in conjunction with thermal barrier coatings.

Some of the costs associated with the use of thermal barrier coatings on industrial gas turbine engines were studied (ref. 18). One of the cases studied compared the operating and maintenance costs of a current production turbine without a thermal barrier coating with the same turbine with thermal barrier coatings on blades, vanes, combustor liners and transition ducts. Turbine inlet temperatures and metal temperatures were the same for each machine and the cooling air flow rate was reduced to improve performance. It was assumed for this case that the thermal barrier coatings would have adequate durability to survive and protect the associated components for two years. For a peaking application (capacity factor 0.12) this would require at least 2100 hours of TBC life, and for a base load application (capacity factor of 0.65), a TBC life of about 12,000 hours would be required. With the two-year life assumption, TBC component removal, inspection, stripping and reapplication would be conducted during a routine biennial turbine inspection in which the turbine casing would be opened. Thermal barrier coating stripping and recoating were estimated (by NASA) to be (mid-1975 \$):

combustor liner	\$100 each
transition piece	\$200 each
stationary vanes	\$150/airfoil
rotating blades	\$150/airfoil

Based on these assumptions, the increased operating and maintenance costs associated with applying and maintaining thermal barrier coatings on these components amounts to 0.391 mills/kWhr for the peaking application, and 0.048

mills/kWhr for the baseload application. These costs represent approximately 25 to 50 percent of the cost of replacing turbine airfoils biennially.

As a result of certain "geopolitical" considerations, the cost of various "critical" materials has risen dramatically in the recent past (1974-1980). Figure 27 (ref. 22) illustrates the price of cobalt, chromium and tantalum over this time period. The price of other alloy materials may also be controlled by "geopolitical" considerations, rather than strictly economic considerations. It is estimated that this dramatic increase in cost of cobalt shown would increase the cost of a hypothetical 100 MW gas turbine engine by about \$450,000 (an increase of about 3 percent in the capital cost of the system). The cost of applying TBC to the cooled airfoils and combustor hardware would be somewhat less than this initially (about \$150,000 - 1979 \$), but periodic stripping and reapplication would be required, as discussed above. Over the lifetime of the turbine, total costs would probably be about the same for either option in the absence of further dramatic price increases beyond inflation. Summarizing the comparison of costs, at the present time, there appears to be no large cost advantage for either option:

(1) Utilizing conventional super-alloys that are becoming more expensive as a result of "geopolitical" considerations.

(2) Substituting alloys with lower contents of critical materials and protecting the hot section parts with thermal barrier coatings. It may be advantageous to the nation, however, to achieve less vulnerability to the supply of critical materials without a cost penalty.

In addition, qualification of a thermal barrier coating system in a production gas turbine system is expected to take a long time. Other factors, such as potential impact damage, inspection (NDE) and reapplication of ceramic coatings must be considered before TBC technology may be considered ready for the utility gas turbine market.

### SUBTASK 3.3 - FUEL/STACK/TEMPERATURE/PERFORMANCE STUDY

The effect on combined cycle performance of constraining the stack gas temperatures to levels high enough to avoid acid corrosion when burning high sulfur content fuels was studied. Results are presented in reference 22 and summarized herein. The use of fuels containing sulfur requires that the cold-end heat exchanger surface and exhaust stack gas temperatures be kept above the sulfuric acid condensation temperatures. A high sulfur content fuel means a high acid concentration which then requires a high stack inlet temperature. Raising the exhaust stack gas temperature, however, results in lower combined cycle efficiency compared to that achievable by a combined cycle burning a sulfur-free fuel. Dew points were estimated as a function of fuel sulfur content and gas turbine design parameters. An equation based on experimental data was used for these dew points calculations. The effect on combined cycle efficiency was determined for air-cooled and water-cooled gas turbine/combined cycles. Combined cycle performance calculations were done first assuming a sulfur-free fuel, and then for a fuel with 0.8 percent sulfur content by weight. This is the maximum sulfur content for a liquid fuel that can be used without sulfur dioxide emission control devices and still meet environmental regulations.

The maximum differences found between the combined cycle performance using sulfur-free fuel and using the 0.8 percent sulfur fuel, was less than one percentage point in efficiency.

The combined cycle performance gains obtained by using thermal barrier coatings (TBC's) in gas turbine blades was previously presented in reference 21. The performance calculations in this report, however, did not take into account the use of high sulfur fuel oils and the corresponding efficiency losses as mentioned above. When included in the analysis, the combined cycle efficiency gain of using TBC with a high sulfur fuel compared to a sulfur-free fuel fired combined cycle without TBC is 0.6 to 1.0 percentage points for the air-cooled gas turbine/combined cycles and 1.6 to 1.8 percentage points for the water-cooled gas turbine/combined cycles. Therefore, TBC's have the potential of allowing the use of the dirtier, less expensive, high sulfur fuels in gas turbines with an increase in efficiency. Without a TBC, the use of a dirtier, less processed fuel would require a reduction in gas turbine inlet temperature and, hence, a reduction in efficiency.

#### 4.0 - CATALYTIC COMBUSTION STUDIES

Catalytic combustion has been demonstrated with low-nitrogen distillate fuels to achieve very low  $\text{NO}_x$  emissions along with high combustion efficiency. The purpose of this task is to demonstrate catalytic combustion with alternative fuels and to identify problem areas associated with the catalytic combustion of these fuels.

##### SUBTASK 4.1 - FIVE-ATMOSPHERE ENDURANCE TEST

The purpose of this subtask was to experimentally determine the durability of a catalyst burning No. 2 distillate oil at a combustion temperature of 1533 K (2300° F) for 1000 hours at five atmospheres pressure. The testing was conducted under contract at Engelhard Industries, Inc. and the results are presented in reference 23. Prior to the contract, the catalyst had been tested for 1000 hours at one atmosphere pressure and little degradation of performance was observed. The five atmosphere tests were conducted at simulated gas turbine steady-state operating conditions, using an air preheat temperature in the range of 663 to 723 K (734 to 842° F), an inlet reference velocity of 14 m/sec (46 ft/sec), and an adiabatic flame temperature of the fuel/air mixture of 1533 K (2300 F).

The performance of the catalyst core was determined by monitoring emission throughout the test, periodically examining  $\text{CO}$ ,  $\text{NO}_x$  and UHC emissions and, at the beginning and end of the test, evaluating the performance of the catalyst using No. 2 diesel fuel over a wide parametric range of test conditions.

Combustion efficiency declined continuously from 99.95 percent at the start of testing to 90 percent after 1014 hours. Initial and final emissions results are summarized below:

	Initial After 03 hr	After 1014 hr	After 1062 hr
Unburned Hydrocarbons (ppm)	0	146	0
Carbon Monoxide (ppm)	30	2420	35
Nitrogen Oxides (ppm)	5.7	5.6	4.3

After the 1014 hours of testing, an unplanned 48 hour, 673 K (752° F) air soak was conducted while analytical system repairs were made. Apparently as a result of this air soak, the catalyst deactivation, which occurred gradually during the life test was reversed. As a result, the final performance tests showed only a slight degradation in catalyst performance. The reason for this sudden improvement in performance is not fully understood. Additional testing is required to demonstrate catalyst durability with thermal cycling, as well as, temperature aging while using larger diameter test sections, 7.5 to 15 cm (3 to 6 in.).

#### SUBTASK 4.2 - PREVAPORIZED FUEL TESTS

An in-house investigation of catalytic combustion using heavy fuels was initiated in FY 1979. The study was intended to examine catalytic combustion with three different fuels: (1) residual fuels, (2) coal-derived liquid fuels, and (3) coal-derived gaseous fuels.

Residual Fuel - Residual fuel tests performed during FY 1980 were primarily concerned with finding ways to eliminate the upstream-burning problem which had been identified in FY 1979. The ignition of the fuel in the premix section of the duct was thought to result from autoignition of the fuel in the heated air stream or from surface ignition of the fuel on the duct walls. Tests were performed in the test section shown in figure 14. A multiple-air-assist fuel injector (fig. 15) was fabricated and tested to see if improved atomization might help to eliminate the preburning. Although this injector produced a very fine mist of fuel, combustion in the premixer still occurred at an inlet-air temperature of 600 K (620° F), the standard test condition. This upstream burning was now observed to be non-continuous, and was broken by approximately 10 minute intervals during which no combustion was observed in the premixer. The conclusion was reached that about 10 minutes was required to deposit sufficient fuel on the duct walls to ignite; once this wall-deposit was burned off, upstream combustion was extinguished until sufficient time elapsed for the deposits to build up again.

One way to avoid deposition of fuel on the walls is to increase the wall temperature. This was done by increasing the inlet-air temperature. With an inlet-air temperature of 750 K (890° F), occasional upstream burning was observed. At an inlet-air temperature of 800 K (980° F), however, stable combustion was achieved with no upstream burning.

Catalytic combustion data with residual fuels were taken with inlet-air temperatures of 800 to 1000 K (980 to 1340° F), using a multiple hex-tube fuel injector. One of the 19 injector modules is shown in figure 16. Equal quantities of fuel were introduced into each of the 19 air passages through a cooled fuel tube as shown.

Combustion efficiency data obtained with an inlet-air temperature of 800 K (980° F) and with a graded-cell catalytic reactor (honeycomb cells) are shown in figure 17. The graded-cell reactor is one with large cells (approximately 1/4 in. diameter) at the inlet and smaller cells (approx. 1/16 in. diameter) at the exit of the reactor. This configuration evolved to prevent the blockage of the small cells by unburnt fuel. It is surmised that radiation losses at the inlet face of the reactor caused local cooling and subsequent incomplete fuel combustion. The combustion efficiency is presented as a function of the adiabatic reaction temperature with curves for constant approach reference velocities of 10, 15, and 20 m/s (33, 49, and 66 ft/sec). Combustion efficiencies approached 100 percent for reaction temperatures

above 1350 K (1970° F) for an approach reference velocity of 10 m/s (33 ft/sec), 1375 K (2015° F), for 15 m/s (49 ft/sec) and 1400 K (2060° F) for 20 m/s (66 ft/sec).

The conversion of fuel nitrogen to  $\text{NO}_x$  is shown in figure 18. Conversion increased with increasing reaction temperature. Forty (40) percent conversion was the maximum observed, and this represents a  $\text{NO}_x$  concentration of about 85 ppm.

The residual fuel tests showed that it may be difficult to operate a lean premixed combustion system, such as that required for catalytic combustion, at inlet-air temperatures below 800 K (980° F). Successful and efficient catalytic combustion can, however, be achieved at inlet-air temperatures of 800 K (980° F) and above and  $\text{NO}_x$  emissions low enough to meet new source standards of 125 ppm are possible.

**Coal-Derived Liquid Fuels** - In-house catalytic combustion testing of three grades of coal-derived liquid (see Table IV) was completed in FY 1980. Tests were performed in the test section shown in figure 14 and results were reported in DOE/NASA/10350-21, (ref. 24). Test conditions included inlet-air temperatures of 600 to 800 K (620° to 980° F), a pressure of  $3 \times 10^5$  Pa (43.5 psia) and reference approach velocities of 10 to 20 m/s (33 to 66 ft/sec).

The first tests were performed using the small-cell catalytic reactor described in Table V(a). The fuel was a naphtha-grade CDL. The inlet-air temperature was 600 K (620° F). The small cells quickly plugged at the inlet face of the reactor as fuel deposited on the surface. It is believed that radiation heat losses from the inlet face of the reactor lowered the surface temperature and subsequent catalyst activity. No further testing of this catalyst configuration was attempted.

Subsequent tests used the graded-cell catalytic reactor described in Table V(b). The graded-cell reactor has large cells at the inlet because large inlet cells have more mass and have been shown to operate with higher surface temperatures than fine cells (ref. 25). The larger cells are also not as easily blocked by fuel deposits on the catalyst surface. The graded-cell reactor worked well with both the naphtha and the middle-distillate fuels at an inlet-air temperature of 600 K (620° F) inlet-air temperature. When the inlet-air temperature was increased to at least 700 K (800° F), the mid-heavy blend could also be reacted without catalyst plugging.

The combustion efficiencies of the three coal-derived liquid fuels are given in figure 19 as a function of the adiabatic reaction temperature for a reference velocity of 10 m/s (33 ft/sec). Also shown for comparison are data from tests with No. 2 diesel fuel. The best performance was obtained, with the naphtha fuel which had combustion efficiencies approaching 100 percent for reaction temperatures greater than 1250 K (1790° F). The middle distillate required reaction temperatures about 75 K (135° F) higher than those for naphtha to achieve the same combustion efficiency. Performance with the middle distillate was very much like that of the No. 2 diesel. The mid-heavy blend required a further increase of approximately 50 K (90° F) to maintain combustion efficiency comparable to that of the middle distillate or No. 2 diesel.

A change in catalyst performance was observed during the tests. Initial tests were made with the No. 2 diesel (labelled "Run A" in figure 19) to establish a baseline. These tests were followed by tests with naphtha, mid-heavy blend, No. 2 diesel ("Run B"), middle distillate, and No. 2 diesel ("Run C") fuels. From the initial No. 2 diesel test ("Run A") to the final ("Run C"), the combustion temperature had to be increased (by increasing fuel/



air ratio) by about 25 to 50 K (45 to 90° F) in order to achieve the original combustion efficiency. Clearly, the long-term effects of operating with coal-derived liquids need to be studied before a decision can be made with regard to the use of catalytic combustors with these fuels.

The conversion of fuel nitrogen to  $\text{NO}_x$  for the three coal-derived liquids is given in figure 20. Conversion rates increased with increasing reaction temperature and were as high as 75 percent. The naphtha had higher conversions than either the middle distillate or mid-heavy blend at any reaction temperature. If the results were compared at the respective reaction temperatures which provided combustion efficiencies near 100 percent, however, there was little difference in the conversions for the three fuels.  $\text{NO}_x$  concentrations at conditions giving high combustion efficiency ranged from 160 ppm for the naphtha to about 300 ppm for the mid-heavy blend. These values were well in excess of the 125 ppm new-source standards. Thus, lean catalytic combustion of coal-derived liquids is apparently not a viable low- $\text{NO}_x$  combustion technique for the particular catalyst and geometry tested.

Coal-Derived Gaseous Fuels - In FY'80 an increased emphasis was placed on the possible utilization of low and medium Btu coal-derived gases as the primary fuels for combined cycle applications. In response to this intent contracts are expected to be signed with Westinghouse and GE to perform combustion tests of NASA-supplied catalytic combustor hardware at their existing gasifier sites. Testing will be completed in FY 1981.

#### SUBTASK 4.3 - LIQUID SPRAY COMBUSTOR TESTS

The objective of these tests was to determine if there was a difference in performance if small (less than 30 microns diameter), or large (70 to 120 microns), fuel droplets were to enter the catalytic reactor as compared to the situation tested in-house in which the fuel was completely vaporized. Two contracts were awarded for this effort: A contract with UTRC was signed in July 1979, and a GE contract was signed in October 1980.

The UTRC testing was performed in a 7.5 cm (3 in.) diameter test rig. A graded-cell catalytic reactor supplied by Acurex was tested using a multiple-source fuel injector. The major problem encountered was that of burning upstream of the catalytic reactor even with inlet-air temperatures as high as 840 K (1053° F). Because of this problem, it was not possible to test with an incompletely vaporized fuel-air mixture. Some data, however, were taken with blends of 20 percent residual fuel with 80 percent No. 2 diesel. Testing will be completed early in FY 1981 and the final report will be published in latter FY 1981.

The GE tests were made in a 12 cm (4.7 in.) diameter duct using a single air-assist fuel injector. The catalytic reactor was supplied by Engelhard. Initial tests were made with a five-cell reactor which tended to plug with fuel deposits even with inlet-air temperatures as high as 870 K (1107° F). A second series of tests using a graded-cell reactor were successful. Stable combustion without upstream burning and no catalyst plugging was obtained for inlet-air temperatures as low as 800 K (980° F). No upstream burning was observed as long as atomizing-air pressure was maintained fairly high to give small fuel droplets. Upstream burning was experienced when large fuel droplets were produced. It is surmised that an enriched fuel/air ratio surrounds the large droplets and higher fuel/air ratios tend to autoignite.

As with the UTRC tests, the high inlet-air temperatures required for successful operation precluded testing with an incompletely vaporized residual fuel. The results suggest that complete vaporization is necessary to avoid fuel deposition on the catalyst surface with this fuel.

Testing will be completed and a report published in FY 1981.

### SUMMARY OF RESULTS

This project addresses the critical research and advanced technology requirements considered necessary for the utilization of coal-derived fuels in utility/industrial applications of advanced gas turbines. The technology efforts included combustion and materials development and system studies to support the developments. This report summarizes the technical progress attained on the project through FY 1980.

Most of the planned laboratory and testing activities have been successfully completed and reports covering these tasks are being written or have been published. A few tasks remain to be completed. These include: the in-house testing of a two stage, variable geometry, combustor sector; the catalytic reactor testing of incompletely vaporized residual fuel oil (two contracts); and the catalytic combustion of coal-derived gases obtained from on-site coal gasifiers (two contracts).

Significant accomplishments of this project include the following:

- (1) A preliminary literature survey of the properties of coal-derived liquids has been published. An updated survey is in progress.
- (2) A two stage combustor emissions model has been developed and utilized to predict the effects of combustor operating conditions and geometry on the conversion of fuel-bound nitrogen (FBN) into oxides of nitrogen ( $\text{NO}_x$ ).
- (3) Rich-lean, two stage, flame-tube combustion tests have successfully demonstrated the capability of this combustor concept to reduce the conversion of FBN to  $\text{NO}_x$ .
- (4) Doped fuel tests have been successfully conducted to study the corrosion effects of known fuel and air contaminants at various concentrations and temperature levels to determine the possible effects of hot corrosion of turbine materials.
- (5) An empirically derived computer program has been developed to analytically predict hot corrosion attack of conventional turbine alloys.
- (6) Barium and strontium have been identified as additives with great potential for reducing hot corrosion caused by sodium sulfate. The intermittent application of these additives has also been identified as a viable approach to the use of these additives in limiting hot corrosion while preventing an excessive buildup of the inert sulfate.
- (7) Actual fuel tests with SRC-II naphtha fuel and a micronized coal-oil mixture demonstrated that both fuels caused excessive deposition and fouling of turbine airfoils and verified that no potential for hot corrosion exists for these fuels.
- (8) An equilibrium thermodynamic analysis was performed using a modified Lewis Complex Chemical Equilibrium Calculation Program to predict successfully the composition and dew points of the deposits formed from the combustion of coal-derived fuels.
- (9) The potential of cooling-hole plugging of film-cooled turbine airfoils when exposed to the combustion products of a typical solvent refined coal-light organic liquid fuel and an SRC fuel plus phosphorus was investigated. It was shown that excessive coolant air mass flow would probably be required to assure the elimination of hole plugging when using these fuels.

(10) Advanced thermal barrier coating (TBC) systems were tested and evaluated. The durability of TBC systems exposed to a Na + V doped combustion flame was significantly increased by decreasing the TBC thickness. Bond coat compositions were shown to have a significant effect on coating system life. Several improved bond coatings were tested and evaluated.

(11) TBC life criteria for coatings exposed to Na + V doped combustion gases were investigated. Coating failures and failure locations were determined to be a function of the thermodynamic dew points and melting points of the contaminants and of the temperature distributions within the coatings.

(12) Bond coat optimization tests were conducted to ascertain the durability of bond coats to oxidation and the durability of bond coats with thermal barrier coatings in a dirty fuel environment, Jet A + (5 ppm Na + 2 ppm V fuel equivalence). Improvements in TBC systems resulted from increased bond coat thicknesses, controlling yttrium content of the coatings, providing sufficient surface roughness of the bond coat to obtain better adherence of the TBC, and from modifying the plasma spraying parameters to include higher power levels and a 3.5 volume percent hydrogen gas in the argon cover gas.

(13) Support studies were conducted to determine the reaction of candidate TBC powders with gas turbine combustion products and with bond coating elements. Potentially benign and harmful reactions were identified and an understanding of the basic material reactions at planned service conditions was gained.

(14) A study was conducted to investigate the effect on performance of thermal barrier coatings when used on advanced steam- and water-cooled gas turbines in combined cycle applications. For the water-cooled cases, the maximum combined cycle efficiency increase was 2.2 percent with a TIT of 1684° C (3062° F) and a TBC of 0.076 cm (0.030 in.) as compared to no TBC at the same TIT. The maximum specific power improvement is 36.6 percent when the TIT is increased from 1449° C (2639° F) to 1733° C (3150° F). Metal substrate temperature was limited to 538° C (1000° F) for this analyses.

(15) A preliminary study was undertaken to identify and quantify the potential cost savings that could result if TBC on gas turbine hot section components permitted the decreased use of strategic alloys in these components. The results of the study indicates that today's turbine hot section components costs are comparable to that cost associated with using TBC on nonstrategic materials and providing for the periodic stripping and reapplication of the TBC. It is noted, however, that it may be advantageous to the nation to develop this capability and decrease vulnerability to outside influences.

(16) Acid corrosion of equipment downstream of the gas turbine when using high sulfur fuels was identified as a possible problem in combined cycle operation. A study was performed on air-cooled and water-cooled gas turbine combined cycle systems to investigate the effect on cycle performance when constraining stack gas temperature to levels high enough to avoid acid condensation. Cycle calculations using TBC's and sulfur-free and 0.8 percent sulfur content (by weight) fuel were performed. Thermal barrier coated air-, steam- and water-cooled gas turbine-steam turbine combined cycle systems were investigated. In all of the cases considered, the maximum combined cycle efficiency difference was less than 1 percent between results obtained for the sulfur-free and 0.8 percent sulfur fuels.

(17) A catalytic reactor endurance test of 1000 hours at 5 atmospheres using No. 2 distillate oil was conducted under contract. A significant deterioration of performance was experienced during the test. The performance was

restored after an inadvertent exposure of the catalyst to air at high temperature. The reason for these changes in performance are not fully understood; however, the ability of the catalyst to regenerate is encouraging. Additional endurance testing, including thermal cycling, is necessary to better define this system.

(18) Catalytic combustion tests of heavy fuels, residual, and coal-derived liquids were conducted in-house. Results of the tests for residual fuel indicate that at inlet air temperatures less than 800 K (980° F) burning of the fuel upstream of the catalyst could be a problem. For coal-derived liquids, the conversion of fuel bound nitrogen produced NO<sub>x</sub> emissions in excess of new source standards.

(19) Liquid spray, catalytic combustor tests of residual fuel and residual fuel blends were conducted under contract to investigate the effect of incomplete fuel vaporization on graded cell reactor performance. Test results indicate that complete vaporization of the fuel and high inlet air temperatures are necessary to prevent upstream burning of deposited fuel and/or plugging of the reactor.

#### FY 1980 PUBLISHED REPORT SUMMARY

The following reports were published during FY 1980 for the CkT project:

- o A conference report was presented describing thermal barrier coating activities, "NASA Progress on Ceramic Coatings for Industrial/Utility Gas Turbines," pp 667-679, Proceedings of the First Conference on Advanced Materials for Alternative Fuel Capable Directly Fired Heat Engines, July 31-August 3, 1979, Maine Maritime Academy, Castine, Maine, December 1979.
- o A Fuel/Stack Temperature/Performance Study, DOE/NASA 2593-17, NASA TM-81531 was completed. The results of this study were presented to DOE at the 10th Quarterly Status Review in Washington, DC, on January 22, 1980.
- o Report DOE/NASA/2593-79/8, NASA TM-79243, "Literature Survey of Properties of Synfuels Derived from Coal," by Reynolds, Thaine W., Neidzwiecki, Richard W., and Clark, John S., was published in February 1980.
- o A report DOE/NASA/2593-79/10, NASA TM-79296 ASME 80-GT-60, "An Analytical Study of Nitrogen Oxides and Carbon Monoxide Emissions in Hydrocarbon Combustion with Added Nitrogen-Preliminary Results" by Bittner, David A., was presented at the 25th International Gas Turbine Conference which was sponsored by the American Society of Mechanical Engineers, New Orleans, Louisiana, March 9-13, 1980.
- o ASME 80-GT-104 DOE/NASA/2593-79/11, NASA TM-79307, "Status of the DOE/NASA Critical Gas Turbine Research and Technology Project," by Clark, John S., prepared for the 25th Annual International Gas Turbine Conference sponsored by the American Society of Mechanical Engineers, New Orleans, Louisiana, March 9-13, 1980.
- o A publication ASME 80-GT-150 DOE/NASA/2593-79/12, NASA TM-79309, "Effect of Sodium, Potassium, Magnesium, Calcium and Chlorine on the High Temperature Corrosion of IN-100, U-700, IN-792, and Mar M-509," by Lowell, C. E. et al., was prepared for the Gas Turbine Conference and Products Show in New Orleans, Louisiana on March 13, 1980.

- o A report, DOE/NASA/2593-79/13, NASA TM-81384, "Effects of Impurities in Coal-Derived Liquids on Accelerated Hot Corrosion of Super-Alloys," by Deadmore, Daniel L. and Lowell, Carl E., was published in March 1980.
- o A report, DOE/NASA/2593-80/14, NASA TM-81469, "Fouling and the Inhibition of Salt Corrosion," by Deadmore, Daniel L. and Lowell, Carl E., was published in April 1980 describing the fuel additive tests.
- o A NASA report, TM-81520, "Evaluation of Hot Corrosion Behavior of Thermal Barrier Coatings," by Hodge, P. E. et al., was presented at the International Conference on Metallurgical Coatings in April 1980, and has been accepted for publication in the Thin Solid Films Journal.
- o A report, DOE/NASA/9416-80/2, NASA CR-159839, "Durability Testing at 5 Atmospheres of Advanced Catalysts and Catalyst Support for Gas Turbine Engine Combustors," by Olsen, B. A. et al., which was performed under contract to Engelhard Minerals and Chemical Corporation was published in April 1980.
- o The final report DOE/NASA/2593-80/15, NASA TM-81472, "Flame Tube Parametric Studies for Control of Fuel Bound Nitrogen Using Rich-Lean Two-Stage Combustion," by Schultz, Donald F. and Wolfbrandt, Gary, was presented at the Western States Section of the Combustion Institute Spring Meeting, Irvine, California, April 21-23, 1980.
- o A report, DOE/NASA/2593-18, NASA TM-81567, "Improved Bond Coatings for Use with Thermal Barrier Coatings," by Gedwill, Michael A., was published in September 1980.
- o A final report, DOE/NASA/2593-17, NASA TM-81531, "Effects on Combined Cycle Efficiency of Stack Gas Temperature Constraints to Avoid Acid Corrosion," by Joseph J. Nainiger of LeRC, was published in July 1980.

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Table I. - COMPOSITION AND PROPERTIES OF SRC-II FUELS. TRACE ELEMENTS ANALYSIS FOR THE NAPHTHA REPORTED IN THIS TABLE WAS FOR A SAMPLE OF FUEL TAKEN AT A POINT IN TIME WHEN THE DEPOSITION/CORROSION TEST HAD BEEN RUN FOR 191 ONE-HOUR CYCLES. TRACE ELEMENT VALUES MARKED WITH AN "\*" ARE CONSIDERED IN THE THERMODYNAMIC PREDICTION OF DEPOSITION.

SRC-II fuel type				
Major elements (weight percent)	Naptha	Light Oil	Wash solvent	Mid: heavy distillate blend
Carbon	84.61 (84.62) <sup>a</sup>	80.45	84.12	86.21
Hydrogen	11.64 (12.09)	9.75	8.80	8.64
Oxygen	3.16 ( 2.33)	9.17	6.34	3.99
Nitrogen	9.61 ( 0.58)	.42	.53	.95
Sulfur	.61 ( 0.38)	.40	.33	.27
Ash	N.D. <sup>b</sup>	N.D.	N.D.	.02
Trace elements (wppm)				
Al	<0.01	<0.01	0.9*	1.0*
B	.08	< .06	< .06	< .09
Ca	< .01	.1*	.6*	.3*
Cl	49.*	<10.	<10.	294.*
Cr	.1*	.04	.06	1.8*
Cu	28.9*	.03	<< .01	< .1
Fe	8.8*	158.*	35.7*	7.0*
K	< .25	.2*	.4*	< .1
Mg	<< .01	.08	.07	.08
Mn	.05	.4	.3	.2
Mo	<< .01	< .01	< .01	<< .01
Na	< .25	.6*	.3*	.5*
Ni	4.8*	.1*	<< .01	.1*
P	<5	<6	<6	<7
Pb	.3*	< .07	< .06	< .04
Si	.09	< .03	.5*	1.1*
Sn	.2	< .06	< .06	< .07
Ti	.03	< .01	.8*	.2*
V	<< .01	< .01	< .2	.07
Zn	10.5*	2.5*	.8*	.1*
Zr	<< .01	< .01	< .02	< .02
Heat of combustion, lower heating value (Btu/lb)	18,497	16,551	16,748	17,590
Chemical composition (vol. percent)				
Aromatics	33.0	43.6	62.0	-
Olefins	6.0	-	-	-
Saturates	61.0	-	-	-
Sp. Gravity 60/60° F	0.824	-	-	0.999
Viscosity, 100° F, cSt	0.816	-	-	4.527

<sup>a</sup>Values in parentheses are analyses provided by the supplier upon shipment of SRC-II naphtha.

<sup>b</sup>N.D. = not determined.



Table II. - COMPOSITION AND PROPERTIES OF COAL-OIL-MIXTURE FUEL (40 WEIGHT PERCENT PITTSBURGH-SEAM COAL IN NO. 2 FUEL OIL)

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Elemental composition (weight percent)

C	82.5	Al	0.65
H	9.5	Ca	.14
N	.6	Fe	.35
O	2.8	K	.028
S	.32	Mg	.024
Cl	.047	Na	.012
Ash	3.7	Si	1.9
		Ti	.042

Trace metals (wppm)

Co	5
Cr	25
Cu	12
Mn	40
Ni	35
Sr	20
V	10
Zr	15

Heat of combustion, higher heating value (Btu/lb)	17,020
Density (g cm <sup>-3</sup> )	1.06
Viscosity, 70° F (centipose)	4000±1000

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Table III. - DEPOSITION AND MATERIAL RESPONSE FROM MACH 0.3 BURNER  
RIG COMBUSTION OF SRC-II FUELS

Comparison of Predicted and Actual Deposit Compositions

	Fuel type (all solvent refined coal liquids (SRC-II))			
	Naphtha	Light Oil	Wash solvent	Mid: heavy distillate blend
Major deposit phases predicted to form (based on trace element chemical analysis of fuel)	Cu <sub>2</sub> O(s) <sup>a</sup> CuO(s) NiFe <sub>2</sub> O <sub>4</sub> (m) Fe <sub>2</sub> O <sub>3</sub> (m)	Fe <sub>2</sub> O <sub>3</sub> (s)	Fe <sub>2</sub> O <sub>3</sub> (s)	Fe <sub>2</sub> O <sub>3</sub> (s) Cr <sub>2</sub> O <sub>3</sub> (m)
Actual deposit collected (identified by X-ray diffraction)	CuO(s) (Cu,Ni,Zn)Fe <sub>2</sub> O <sub>4</sub> (s) (Cu <sub>0.2</sub> Ni <sub>0.8</sub> )O(m)	Fe <sub>2</sub> O <sub>3</sub> (s)	Fe <sub>2</sub> O <sub>3</sub> (s) Fe <sub>3</sub> O <sub>4</sub> (s)	Fe <sub>2</sub> O <sub>3</sub> (s)

<sup>a</sup>s = strong; m = medium

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Table IV. - DESCRIPTION OF FUELS.

	Naphtha	Middle distillate	Mid-heavy blend	Diesel
Distillation, K				
IBP	336	448	443	456
10	356	480	484	497
20	373	490	495	509
50	408	512	522	537
70	431	528	546	556
90	466	549	627	583
FBP	487	578	644	606
Elementals, percent by weight				
Carbon	84.62	85.59	86.21	86.7
Hydrogen	12.09	9.06	8.64	13.0
Nitrogen	.58	.87	.95	.014
Sulfur	.38	.29	.21	.28
Oxygen (by difference)	2.33	4.19	3.99	-----
Specific gravity (28 K)	0.812	0.982	0.999	0.847
Viscosity, cS	0.816 @ 311 K	6.02 @ 296 K	4.527 @ 311 K	3.8 @ 296 K
Gross heat of combustion, J/kg	$4.220 \times 10^7$	$4.020 \times 10^7$	$3.996 \times 10^7$	$4.453 \times 10^7$
Volume percent aromatics	37.1	----	84.3	39.27

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Table V. - DESCRIPTION OF CATALYTIC REACTORS.

(a) Uniform cell reactor.

Element	Catalyst material	Catalyst loading, kg/m <sup>3</sup>	Substrate manufacturer	Substrate material	Cell density, cells/cm <sup>2</sup>	Open area, percent
1	Pt	3.6	Gen. Refractories	Cordierite	34	67
2	↓	↓	↓		↓	↓
3						
4	↓		↓		↓	↓
5	1 Pt/2 Pd		Corning		46.5	63
6	↓		↓		↓	↓
7						
8	↓	↓	↓		↓	↓

(b) Graded cell reactor.

Element	Catalyst material	Catalyst loading, kg/m <sup>3</sup>	Substrate manufacturer	Substrate material	Cell density, cells/cm <sup>2</sup>	Open area, percent
1	Pt/Pd	3.6	Dupont	Mullite	2.6	75
2	Pt/Pd	↓	↓	↓	2.6	75
3	Pd				9.3	60
4	Pd		↓	↓	9.3	60
5	2 Pd/1 Pt		Corning	Cordierite	46.5	63
6	↓	↓	↓	↓	↓	↓
7						
8	↓	↓	↓	↓	↓	↓

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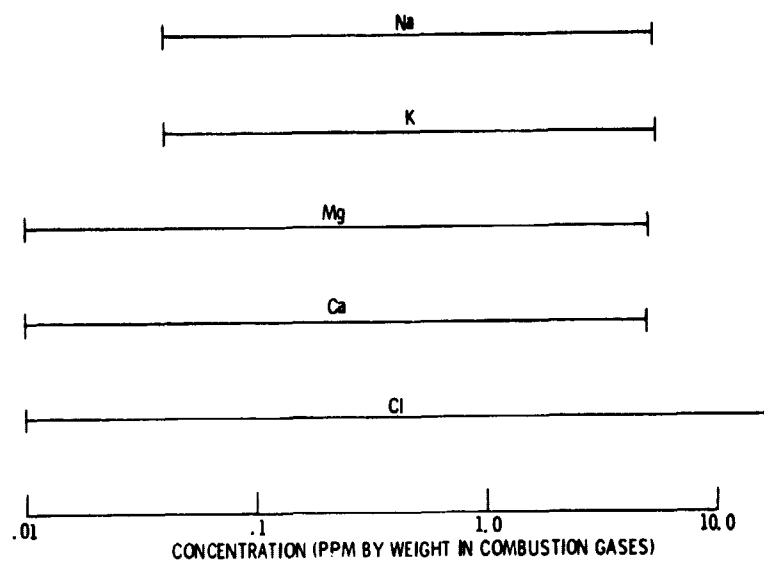


Figure 1. - Impurity range in doped fuel experiment.

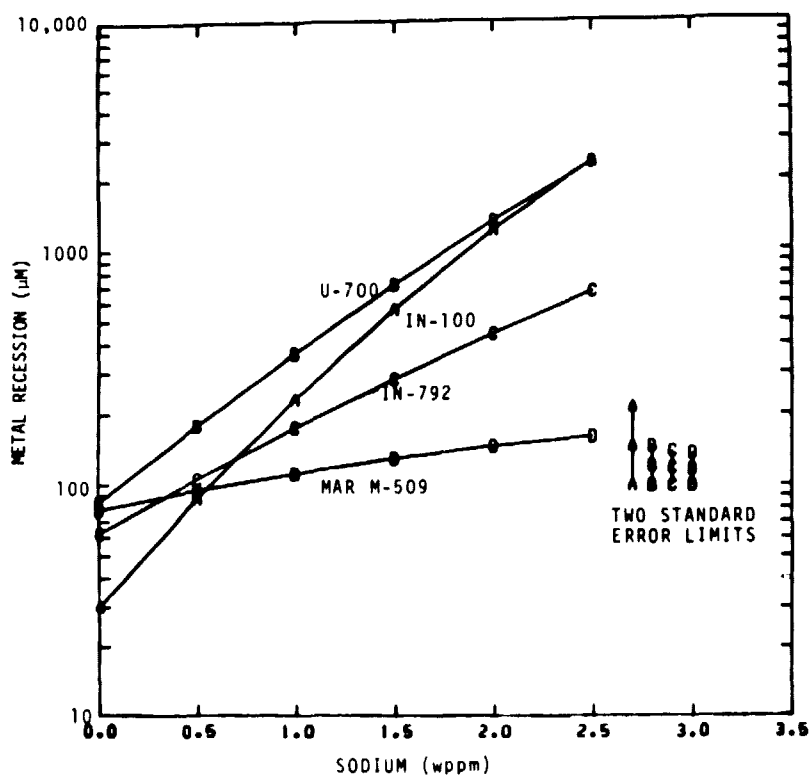


Figure 2. - Hot corrosion attack as a function of sodium concentration. Potassium = 0.9 wppm, magnesium and calcium = 0.10 wppm, chlorine = 2.93 wppm, T = 950°C, and time = 100 hours.

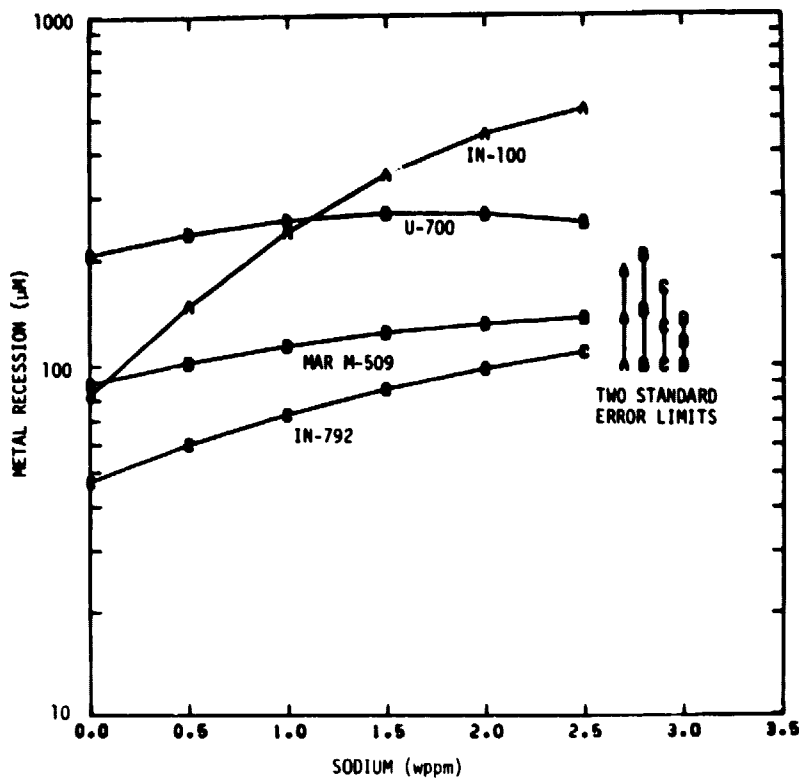


Figure 3. - Hot corrosion attack as a function of sodium concentration. Conditions as for Figure 2, except magnesium and calcium = 1.0 wppm.

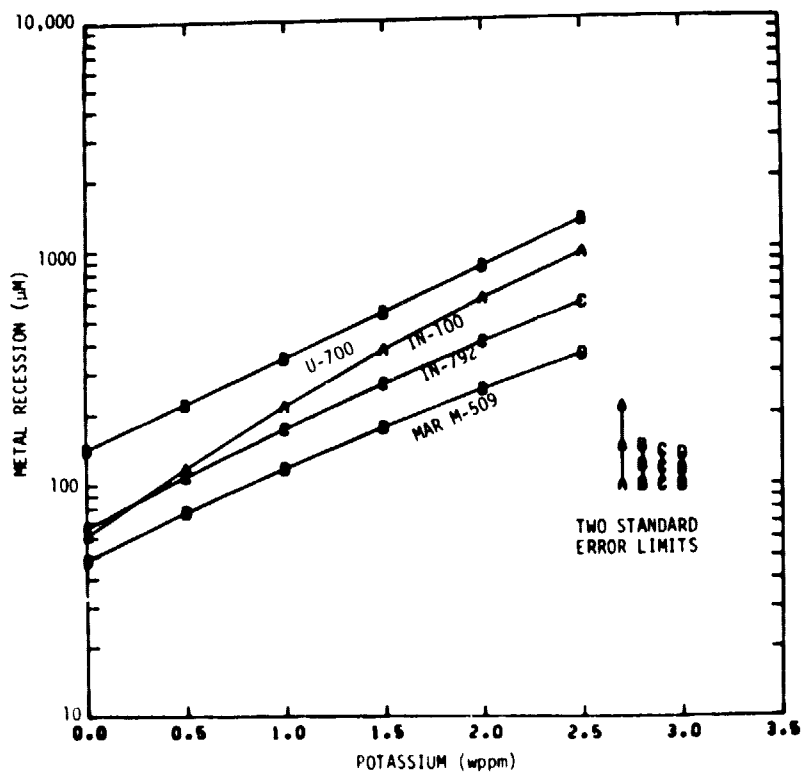


Figure 4. - Hot corrosion attack as a function of potassium concentration. Sodium = 0.9 wppm, magnesium and calcium = 0.1 wppm, chlorine = 2.93 wppm, T = 950°C, and time = 100 hours.

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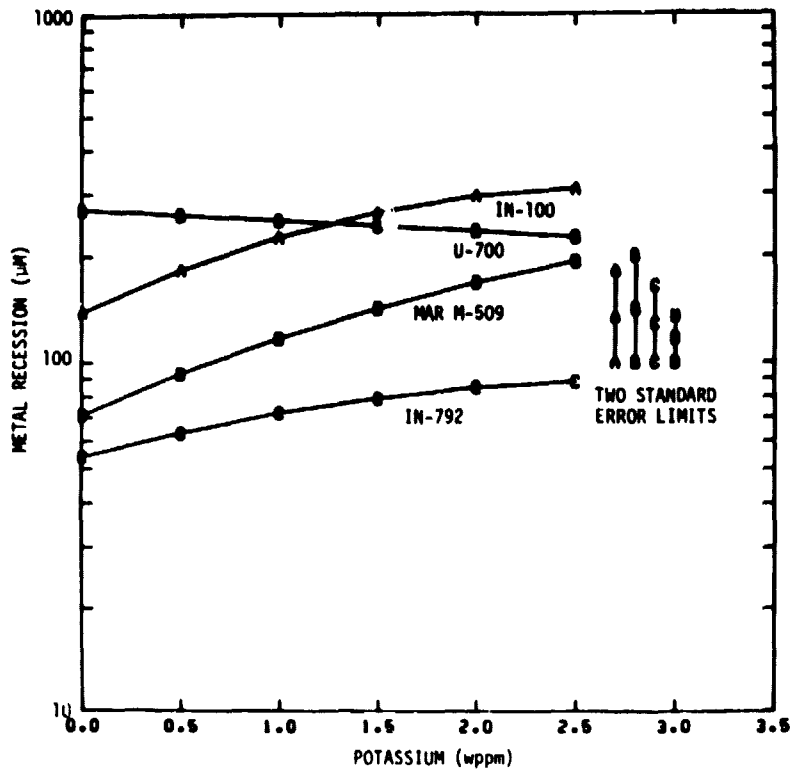


Figure 5. - Hot corrosion attack as a function of potassium concentration. Conditions as for Figure 4, except that magnesium and calcium = 1.0 wppm.

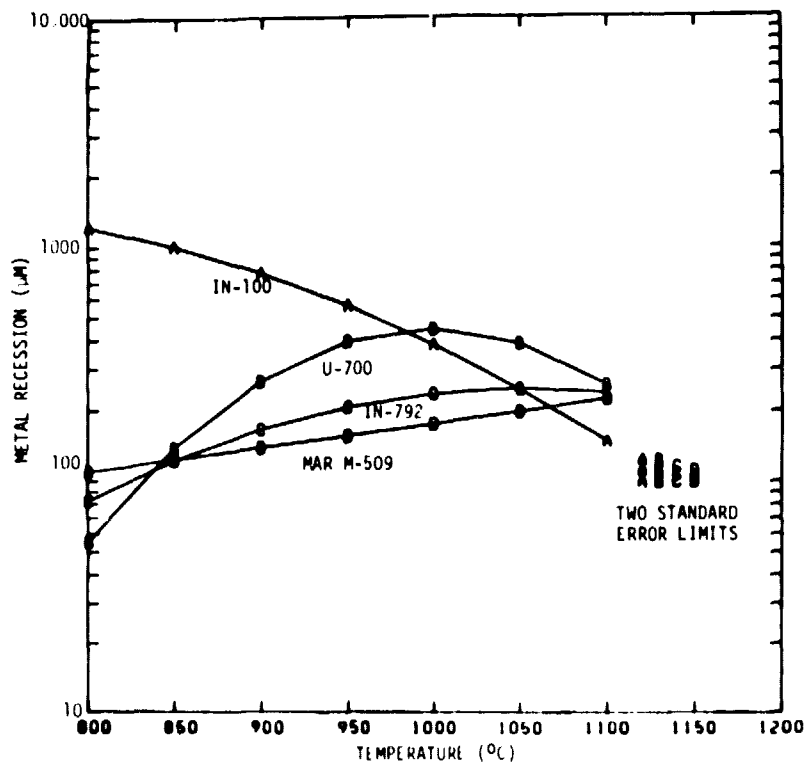


Figure 6. - Hot corrosion attack as a function of temperature. Sodium and potassium = 0.9 wppm, magnesium and calcium = 0.47, and time = 100 hours.

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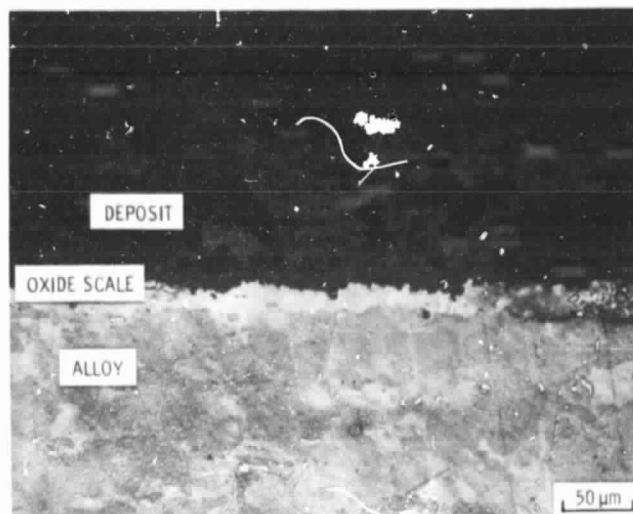


Figure 7. - Deposit morphology on IN-100 exposed in a Mach 0.3 burner rig fueled with SRC-II naphtha.

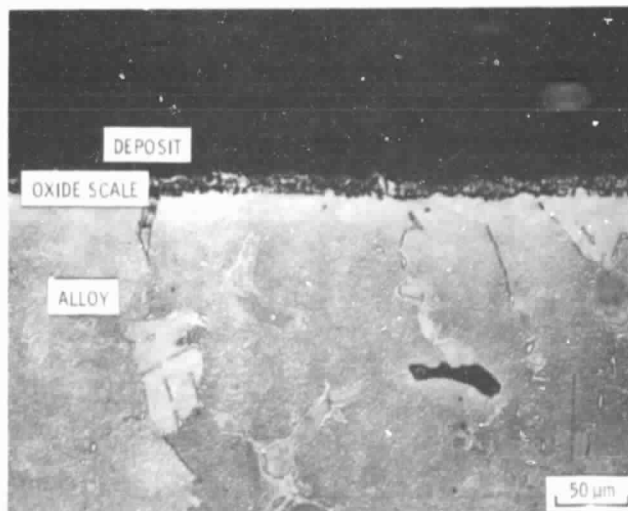
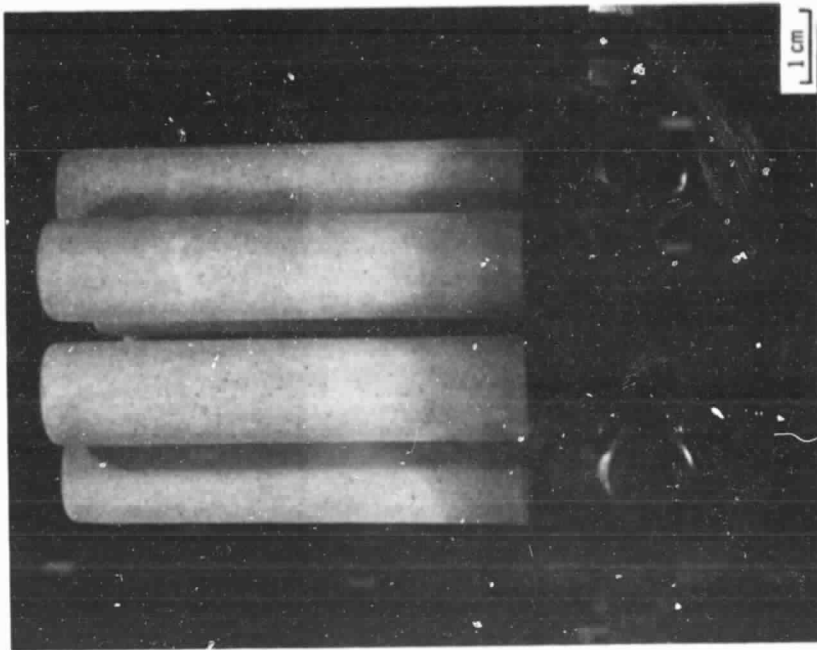


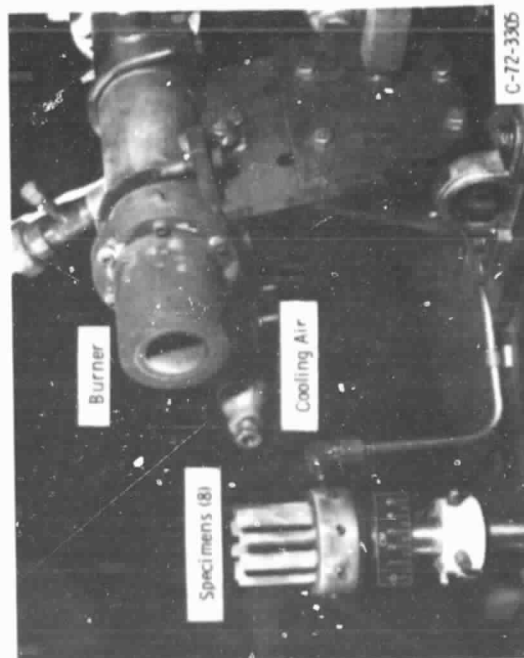
Figure 8. - Deposit morphology on IN-100 exposed in a Mach 0.3 burner rig fueled with a coal-oil mixture.



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(b) Specimen holder assembly.



(a) Overall view.

Figure 9. - Mach 0.3 oxidation apparatus.

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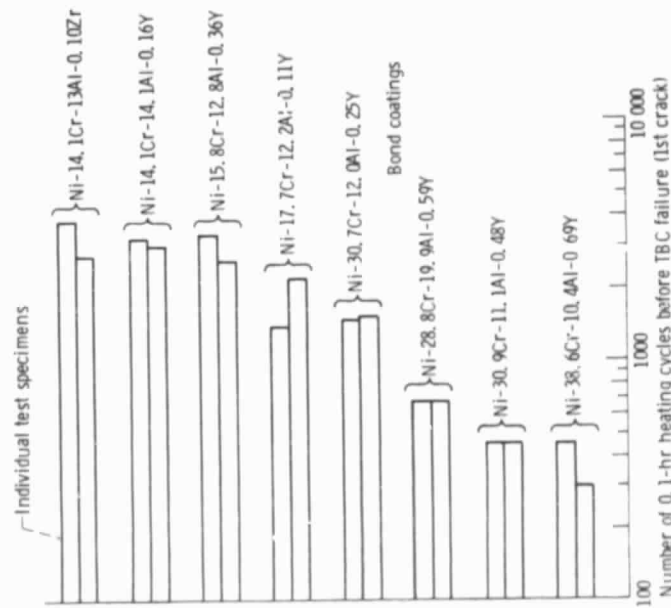
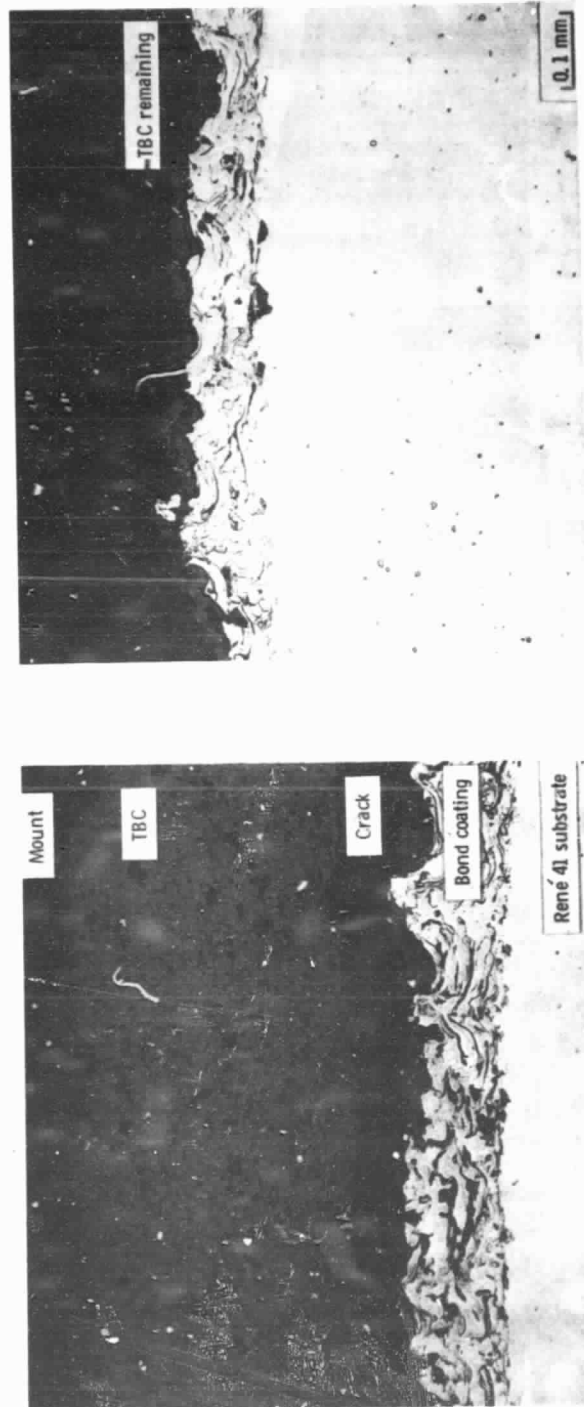


Figure 10. - Performance of TBC systems on solid Rene 41 pins in Mach 0.3 burner rig oxidation.

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(b) Back surface.

(a) Front surface.

Figure 11. - Photomicrograph of  $ZrO_2-12Y_2O_3/Ni-14, 1Cr-13, Al-O, 10Zr$  TBC system,  $\approx 0.015$  cm (0.006 in.) thick bond coating thickness, on René 41 pins after 2748 cycles of oxidation testing in A Mach 0.3 burner rig at 1050°C (1922°F).

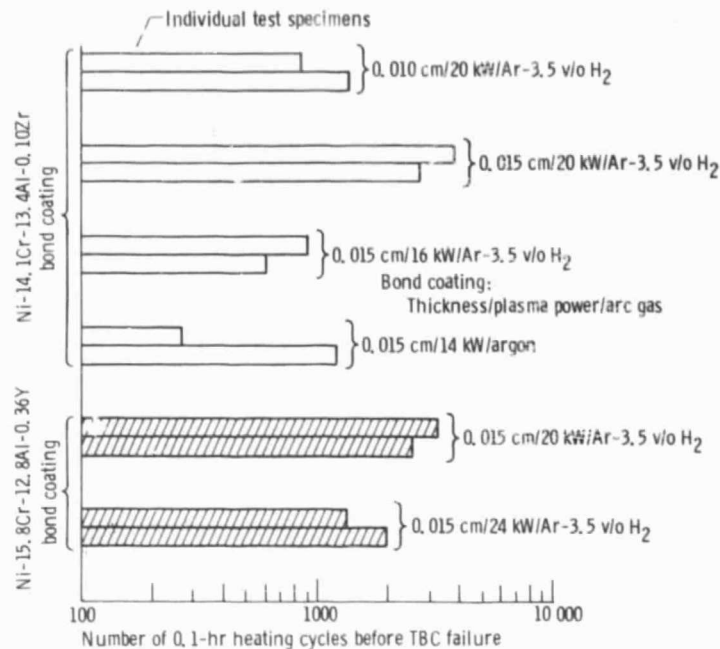


Figure 12. - Effect of bond coating thickness and plasma spraying conditions on performance of  $ZrO_2-12Y_2O_3$  TBC systems on solid Rene 41 pins in Mach 0.3 burner rig oxidation. TBC thickness: 0.038 cm. Maximum exposure temperature at center of pins: 1050° C.

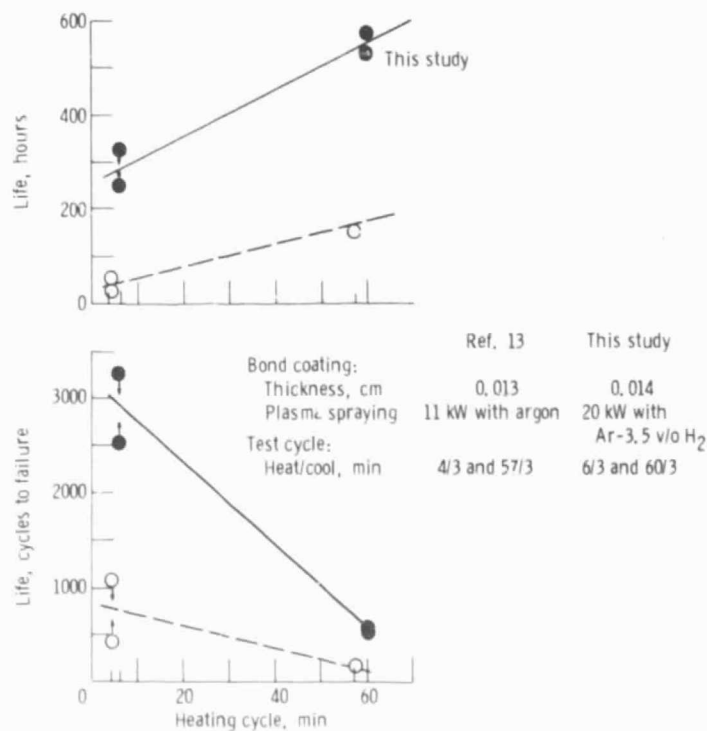


Figure 13. - Effect of cycling frequency on life of TBC  $ZrO_2-12Y_2O_3$  on Ni-15, 8Cr-12, 8Al-0.36Y on solid Rene 41 pins in a Mach 0.3 burner rig at 1050° C.

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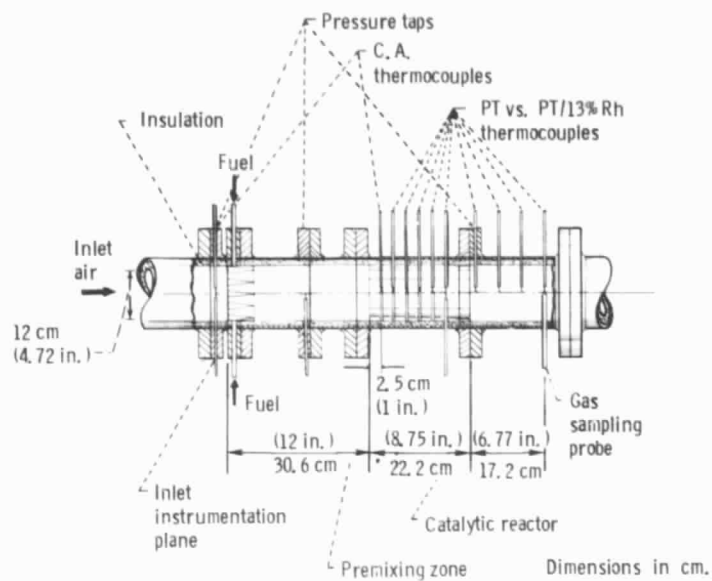
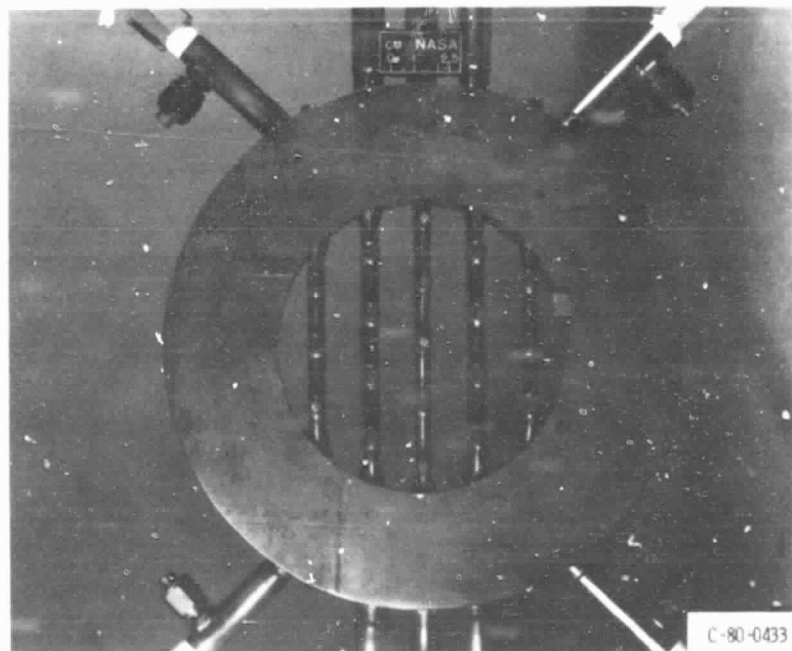


Figure 14. - Test section.



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Figure 15. - Multiple air-assist fuel injector.

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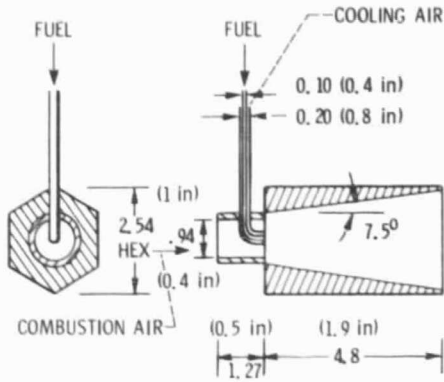


Figure 16. - Hexagonal tube module (one of 19).

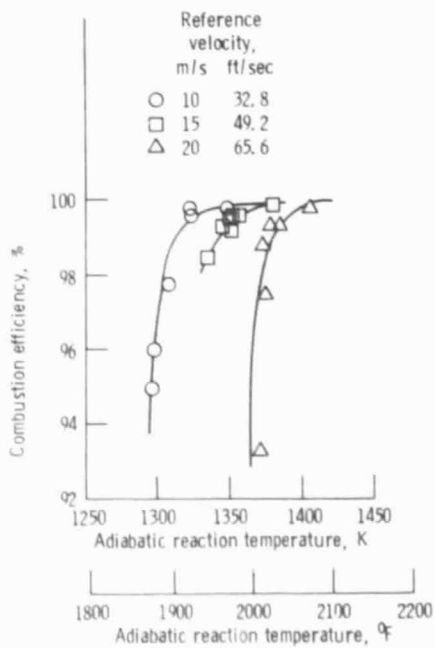


Figure 17. - Combustion efficiency with residual fuel. Inlet-air temperature, 800 K (981°F); pressure,  $3 \times 10^5 \text{ N/m}^2$  (43.5 psia).

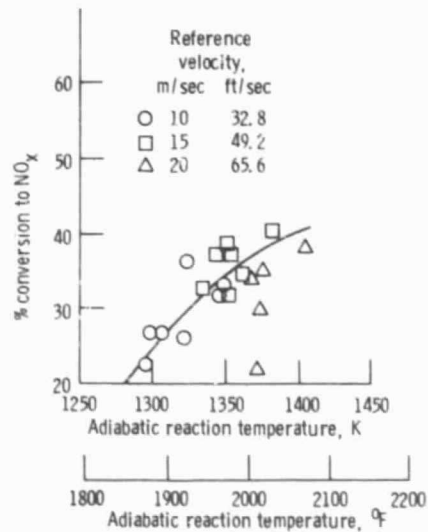


Figure 18. - Fuel nitrogen conversion with residual fuel. Inlet-air temperature, 800 K (981° F); pressure,  $3 \times 10^5$  N/m<sup>2</sup> (43.5 psia).

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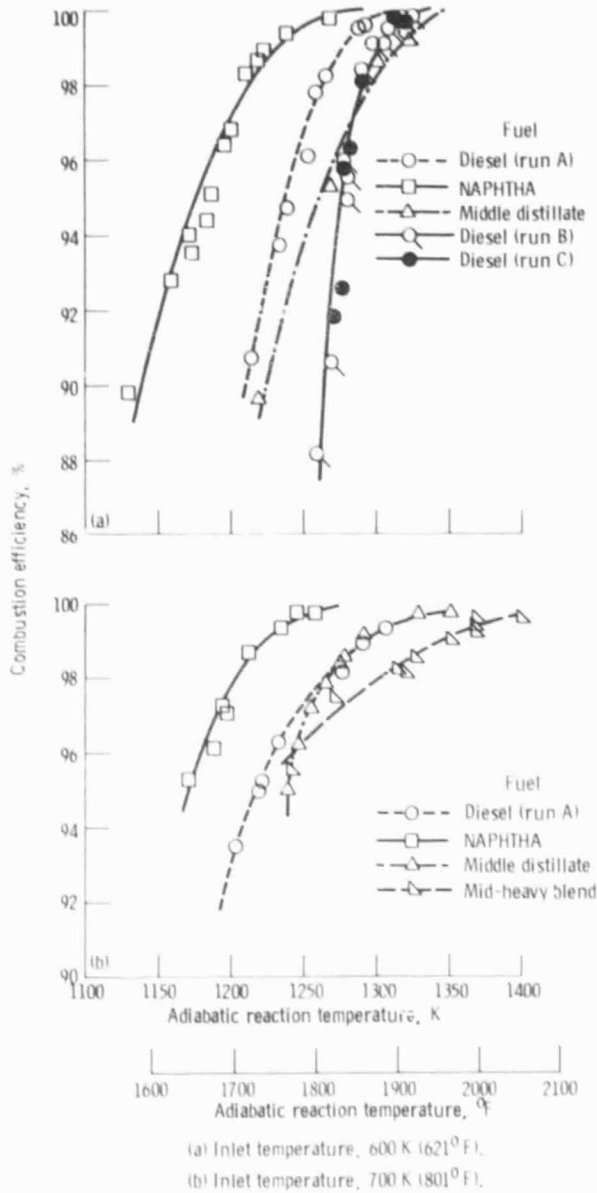


Figure 19. - Effect of fuel type on combustion efficiency. Reference velocity, 10 m/s (33 ft/s); pressure,  $3 \times 10^5$  N/m<sup>2</sup> (43.5 psia).

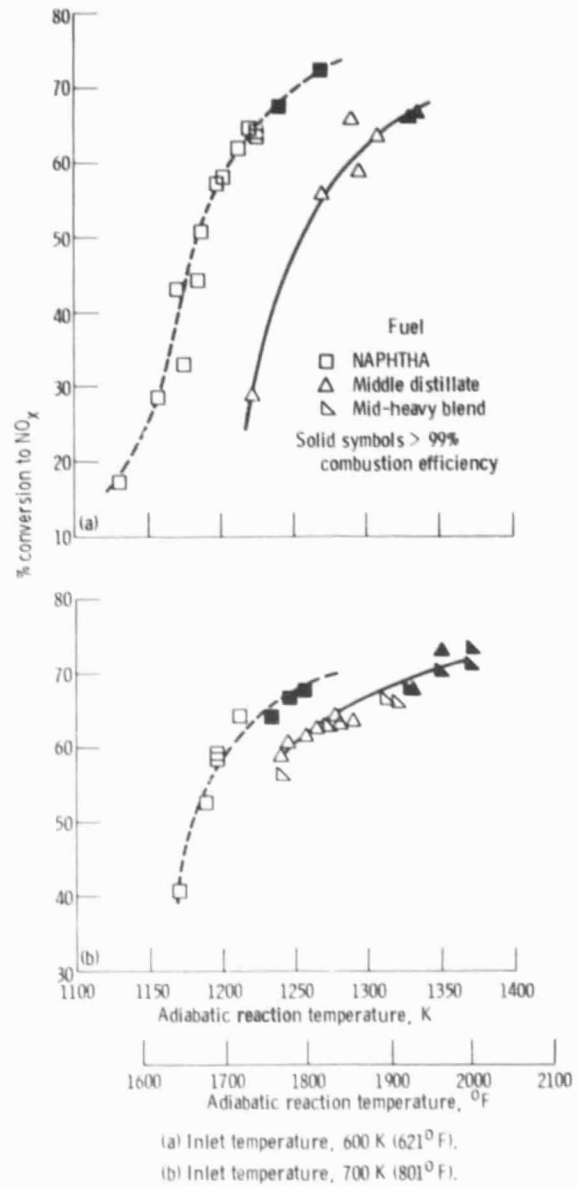


Figure 20. - Effect of fuel on conversion of fuel nitrogen to NO<sub>x</sub>. Reference velocity, 10 m/s (32.8 ft/s); pressure,  $3 \times 10^5$  N/m<sup>2</sup> (43.5 psia).